Lib.

MAR 10 1948

REGISTERED NO. M. 3121

PROCEEDINGS

OF THE

INDIAN ACADEMY

OF SCIENCES

VOL. XXVI] *SECTION A* [NO. 5

NOVEMBER, 1947

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO, SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES, BANGALORE.

SYNTHETICAL EXPERIMENTS IN THE CHROMONE GROUP

Part XXII. Nitroflavones as Intermediates for the Synthesis of Hydroxy- and Hydroxymethoxyflavones

BY NITY ANAND AND K. VENKATARAMAN, F.A.SC.

(Department of Chemical Technology, University of Bombay)

Received July 25, 1947

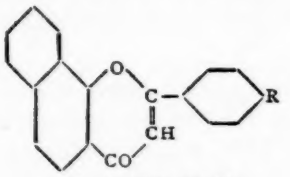
TAKING advantage of the easier removal of O-benzoyl and benzyl groups in comparison with the O-methyl group, partially methylated polyhydroxyflavones such as kæmpferide,[1] isorhamnetin,[1] myricetin,[2] diosmetin,[3] tricin,[4] and rhamnazin[5] have been prepared by using benzoyloxy or benzyloxy derivatives in the acetophenone or acid anhydride reactant, in the Robinson flavone synthesis. The observation,[6] that by the action of aluminium chloride under specified conditions, preferential demethylation in the 5-position takes place in methylated polyhydroxyflavones, has been utilised for the synthesis of 5:8-dihydroxyflavone[7] and several partially methylated polyhydroxyflavones, such as genkwanin,[8] wogonin,[9] tectochrysin[10] and primetin-8-methyl ether.[11] Hydrobromic acid in acetic acid can also be used for the same purpose.[12] It has been found that the 3-methoxyl is also susceptible to demethylation by aluminium chloride and by hydrobromic acid in acetic acid,[12] and this has been used by Seshadri and Venkateswarlu[13] for the synthesis of calycopterin. In connection with the work on calycopterin and rhamnazin, it was observed[12] that hydrobromic acid in acetic acid at room temperature attacked the 5-methoxyl in preference to the 3-methoxyl.

Naturally occurring colouring matters derived from resorcinol and phloroglucinol couple with diazonium salts, and Perkin[14] obtained the disazo dyes. Mahal and one of us[15] prepared from 6-hydroxy-flavone the 5-benzeneazo derivative, which has been reduced, diazotised and hydrolysed to the corresponding dihydroxy compound.[16] While this method has obvious possibilities for the synthesis of polyhydroxyflavones and partially methylated polyhydroxyflavones, an alternative route to the intermediate amines would be through the corresponding nitroflavones. The introduction of a hydroxyl through the diazo coupling reaction has the limitation that the new group can only be located *ortho* or *para* to a hydroxyl group originally present in the 2-phenyl or the fused benzene ring of the flavone

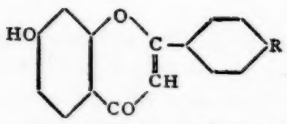
molecule. Proceeding through a nitroflavone there will be a greater latitude regarding the position of the hydroxyl group to be introduced. The exploratory experiments described in the present paper have shown that the method may be utilised for synthesis in the flavone and *iso*-flavone series. Bogert[17] nitrated α-naphthaflavone to a mixture of the 2'-, 3'- and 4'-nitroflavones, which were separated as their amines, the latter being then characterised after diazotisation as their β-naphthol dyes. He also prepared 2'-hydroxy-α-naphthaflavone from the corresponding amine, *via.* the diazo salt. Sugasawa[18] prepared 5-amino-6-hydroxyflavone from the corresponding acetamido compound, but failed to hydrolyse it to the dihydric phenol. Virkar,[19] in a study of the rearrangement of nitroaryl esters, prepared some nitroflavones, which were reduced to the corresponding amines. We have now synthesised 4'-hydroxy-α-naphthaflavone, 7:4'-dihydroxyflavone, 4'-hydroxy-7-methoxyflavone (*iso*pratol) and 5:4'-dihydroxy-7-methoxyflavone (genkwanin), by hydrolysis of the corresponding aminoflavones through the diazo salts, the amines being obtained by the reduction of the nitroflavones.

The diazo salt of 4'-amino-α-naphthaflavone (I, R = NH_2) could be hydrolysed to 4'-hydroxy-α-naphthaflavone (I, R = OH) only by boiling with 30 per cent. sulphuric acid after the complete removal of free nitrous acid.

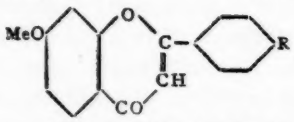
O-Di-*p*-nitrobenzoyl-resacetophenone was rearranged by potassium carbonate and toluene[20] to the diketone, which on cyclicisation gave 4'-nitro-7-hydroxyflavone (II, R = NO_2). It was reduced to the amine (II, R = NH_2), which on diazotisation and hydrolysis as in the previous case, gave 7:4'-dihydroxyflavone (II, R = OH). 4'-Nitro-7-methoxyflavone (III, R = NO_2), prepared by methylation of the corresponding hydroxyflavone, was reduced



(I) R = NH_2 or OH



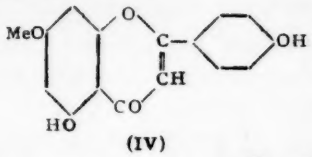
(II) R = NO_2, NH_2 or OH



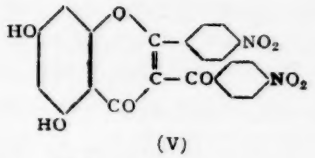
(III) R = NO_2, NH_2 or OH

to the amine (III, R = NH_2), which was diazotised and hydrolysed to 4'-hydroxy-7-methoxyflavone (III, R = OH) (*iso*pratol).

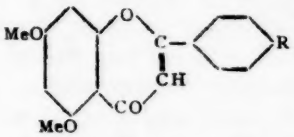
With a view to applying this method for the synthesis of genkwanin (IV), the tri-(*p*-nitrophenyl)-ester of phloracetophenone, prepared by condensing *p*-nitrobenzoyl chloride and phloracetophenone in pyridine under specific conditions, was submitted to rearrangement with potassium carbonate in toluene;[20] but subsequent treatment with concentrated sulphuric acid in the cold, gave 3-*p*-nitrobenzoyl-4′-nitro-5: 7-dihydroxyflavone (V), which could not be hydrolysed to 4′-nitro-5: 7-dihydroxyflavone. When the rearrangement was carried out with sodium ethoxide in alcohol[21] the ester was merely hydrolysed.



(IV)



(V)



(VI) R=NO_2, NH_2 or OH

The *p*-nitrobenzoyl ester of 4: 6-*o*-dimethylphloracetophenone was then prepared; it could not be rearranged to the diketone by means of potassiun carbonate [20] or atomic sodium[22] in toluene, the ester remaining unaffected, but gave the diketone when treated with sodamide[23] in benzene or toluene. This on cyclicisation gave 4′-nitro-5: 7-dimethoxyflavone (VI, R = NO_2), which crystallised in dimorphic forms; on reduction both gave the same 4′-amino-5: 7-dimethoxyflavone (VI, R = NH_2). Diazotisation of the amine and hydrolysis gave the 5-monomethyl ether of genkwanin (VI, R = OH), which on treatment with aluminium chloride[6] in nitrobenzene led to 4′: 5-dihydroxy-7-methoxyflavone (IV) (genkwanin).

The probability that puddumetin, isolated by Chakravarti and Ghosh,[24] from the bark of *Prunus puddum* is identical with genkwanin, has been suggested by one of us.[25] The identity has now been confirmed by taking a mixed melting point of puddumetin and genkwanin synthesised by us.

Experimental

4′-Nitro-α-naphthaflavone (I, R = NO_2)

2-Aceto-1-naphthol-*p*-nitrobenzoate, obtained by heating acetonaphthol (10 g.) in pyridine (40 c.c) and *p*-nitrobenzoyl-chloride (1 mol., 10 g.) for half an hour on the water-bath, crystallised from alcohol or benzene in light

yellow thick needles (16 g.), m.p. 151–52° (Found: N, 4·4. $C_{19}H_{23}O_5N$ requires N, 4·2%) (Virkar,[19] m.p. 151°). The ester (4 g.) in toluene (30 c.c.) and freshly ignited potassium carbonate (12 g.) was refluxed for eight hours, with mechanical stirring, toluene filtered off, the orange red mass washed with benzene, dried and stirred into dilute acetic acid, and the diketone collected (3 g.). It crystallised from acetic acid in yellow thin long needles or from acetone in yellowish orange needles, m.p. 222° (Found: N, 4·0 $C_{19}H_{23}O_5N$ requires N, 4·2%) (Virkar,[19] m.p. 222°). 4′-Nitroflavone, obtained by diluting a solution of the diketone (1 g.) in concentrated sulphuric acid (20 c.c.) after having been kept overnight, crystallised from acetic acid in long thin light yellow plates, m.p. 293° (Found: N, 4·5. $C_{19}H_{11}O_4N$, requires N, 4·4%) (Virkar,[19] m.p. 293°).

4′-Amino-α-naphthaflavone (*I*, $R = NH_2$)

To a boiling solution of the nitroflavone (0·5 g.) in acetic acid (5 c.c.), iron powder (0·5 g.) was added in about one hour's time, refluxed for another half an hour, the unreacted iron filtered, the dark brown solution diluted, and the greenish yellow amine collected. It was crystallised as its hydrochloride from water containing hydrochloric acid in bunches of small orange needles (0·4 g.); when heated it discolours and melts at 250–51° (Found: N, 4·4. $C_{19}H_{14}O_2NCl$ requires N, 4·3%). The amine obtained by neutralising a solution of the hydrochloride with sodium carbonate crystallised from dilute alcohol in long thin light yellow plates, m.p. 265° (Virkar,[19] m.p. 265°, non-crystalline). The yellow solutions in alcohol and in sulphuric acid exhibit a bright green fluorescence.

4′-Hydroxy-α-naphthaflavone (*I*, $R = OH$)

The amine (0·1 g.) was dissolved in water (50 c.c.) containing hydrochloric acid, cooled and diazotised by sodium nitrite (0·03 g.). After keeping at 0–5° for ten minutes, excess of nitrous acid was destroyed by urea, and the diazo solution slowly added to thirty per cent. boiling sulphuric acid (100 c.c.), when some frothing due to the evolution of nitrogen took place, and the diazo solution was almost immediately hydrolysed as shown by testing with alkaline β-naphthol. If a higher concentration of acid was used or there was free nitrous acid, only bye-products were formed. On cooling the solution, light yellow bunches of short needles separated, which were collected, washed free from acid and crystallised from alcohol and acetic acid mixture in small colourless needles (0·05 g.), m.p. 315–16° (Found: C, 78·8; H, 3·9. $C_{19}H_{12}O_3$ requires C, 79·2; H, 4·0) (Kostanecki,[26] m.p. 315–16°). It does not give any colour with ferric chloride, and is turned yellow with concentrated sulphuric acid, giving an almost colourless solution

with a bright green fluorescence, as described by Kostanecki[24] for 4′-hydroxy-α-naphthaflavone.

The *acetate*, prepared by refluxing with acetic anhydride and pyridine, crystallised from acetic acid in long thin colourless needles, m.p. 214° (Found: C, 76·8; H, 4·2. $C_{21}H_{14}O_4$ requires C, 76·4; H, 4·2) (Kostanecki,[26] m.p. 215°). It shows the same behaviour as the hydroxyflavone towards concentrated sulphuric acid.

2-Hydroxy-4-(p-nitro) benzoyloxy-4′-nitrodibenzoylmethane

Resacetophenone-di-(*p*-nitro) benzoate, prepared as in the last case, from resacetophenone and *p*-nitrobenzoyl chloride, was obtained as an amorphous solid from benzene, alcohol or acetic acid, m.p. 151–52° (Found: N, 5·9. $C_{22}H_{14}O_9N_2$ requires N, 6·2%). 2-Hydroxy-4-(*p*-nitro) benzoyloxy-4′-nitrodibenzoylmethane (14 g.) obtained by the rearrangement of the ester (20 g.), as in the last case, crystallised from acetone in yellow plates, m.p. 225–26° (Found: N, 6·0. $C_{22}H_{14}O_9N_2$ requires N, 6·2%).

This on treatment with glacial acetic acid cyclicised, 7-*p*-nitrobenzoyloxy-4′-nitroflavone thus obtained crystallised from acetic acid in bunches of colourless needles, m.p. 294–95° (Found: N, 6·3. $C_{22}H_{12}O_8N_2$ requires N, 6·4%).

4′-Nitro-7-hydroxyflavone (*II*, $R = NO_2$)

The diketone (2 g.) was dissolved in concentrated sulphuric acid (20 c.c.), left overnight, poured over chipped ice, the flavone thus obtained was collected, washed with cold alcohol and crystallised from acetic acid in light yellow, long thin plates (1·0 g.), m.p. 310–11° (Found: N, 5·1. $C_{15}H_9O_5N$ requires N, 4·9%). It gives a reddish brown colour with ferric chloride.

7:4′-Dihydroxyflavone (*II*, $R = OH$)

7-Hydroxy-4′-aminoflavone, obtained by reduction of the nitro flavone (0·5 g.) with iron and acetic acid, as in the last case, crystallised from dilute alcohol in bunches of light yellow curved needles (0·3 g.), m.p. 338–40°, after darkening at 310° (Found: N, 5·4. $C_{15}H_{11}O_3N$ requires N, 5·5%) Its alcoholic solution exhibits a blue fluorescence, and it dissolves in concentrated sulphuric acid, giving an almost colourless solution with a strong blue fluorescence.

7:4′-Dihydroxyflavone, obtained by diazotisation and hydrolysis of the amine (0·35 g.) with 30 per cent. boiling sulphuric acid, crystallised from alcohol in bunches of light yellow needles (0·2 g.), m.p. 315°, not depressed when admixed with a sample which had been prepared by Mahal and

Venkataraman[35] (Kostanecki and Osius,[28] m.p. 315°) (Found: C, 70·7; H, 4·1. $C_{15}H_{10}O_4$ requires C, 70·9; H, 3·9%). It agrees with all its properties with those described for 7:4′-dihydroxyflavone by Kostanecki and Osius.[28]

The *diacetate*, obtained by refluxing with acetic anhydride and pyridine, crystallised from alcohol in colourless needles, m.p. 184° (Kostanecki and Osius,[28] m.p. 184°) (Found: C, 67·4, H, 4·1. $C_{19}H_{14}O_6$ requires C,67·4; H, 4·1%).

4′-Nitro-7-methoxyflavone (*III*, $R = NO_2$)

4′-Nitro-7-methoxyflavone, obtained by methylation of 4′-nitro-7-hydroxyflavone (1 g.), with alkali and dimethyl sulphate in the cold, crystallised from acetic acid in light yellow needles (0·85 g.), m.p. 216–17° (Found: N, 5·0. $C_{16}H_{11}NO_5$ requires N, 4·7%).

4′-Hydroxy-7-methoxyflavone (*Iso*pratol) (*III*, $R = OH$)

The amine, obtained by reduction of the nitroflavone (0·7 g.) with acetic acid and iron powder, crystallised from dilute alcohol in thin light yellow needles (0·5 g.), m.p. 201–02° (Found: N, 5·5. $C_{16}H_{13}O_3N$ requires N, 5·3%). Its light yellow solution in alcohol exhibits a bluish fluorescence, and it dissolves in concentrated sulphuric acid giving an almost colourless solution with a blue fluorescence.

The amine (0·5 g.) dissolved in water (25 c.c.) containing hydrochloric acid, was diazotised and hydrolysed by adding to thirty per cent. boiling sulphuric acid in the usual manner. It crystallised from alcohol in light yellow needles (0·37 g.), m.p. 260°, not depressed by admixture with a sample which had been prepared by Mahal and Venkataraman[37] (Found: C, 71·8; H, 4·4. $C_{16}H_{12}O_4$ requires C, 716; H, 4·5). The melting point of the substance in Mahal and Venkataraman's paper[37] should read as 260°. The alcoholic solution gives brown colour with ferric chloride, and its light yellow solution in concentrated sulphuric acid exhibits a blue fluorescence. On demethylation with hydriodic acid in acetic anhydride it gave 7:4′-dihydroxyflavone.

7:4′-*Dimethoxyflavone*, obtained by methylating with dimethyl sulphate in alkaline solution in the cold crystallised from alcohol in long thin colourless needles, m.p. 149–50° (Kostanecki and Osius[26], m.p. 149°) (Found: C, 72·5; H, 5·2. $C_{17}H_{14}O_4$ requires C, 72·3; H, 4·9%).

7-Methoxy-4′-acetoxylflavone obtained by refluxing with acetic anhydride and pyridine crystallised from alcohol in colourless needles, m.p. 155°C. (Found: C, 69·8; H, 4·6. $C_{18}H_{14}O_5$ requires C, 69·7; H, 4·5%).

Tri-o-(p-nitro)-benzoyl phloracetophenone

Phloracetophenone (3·4 g.) was dissolved in pyridine (40 c.c.) and *p*-nitrobenzoyl chloride (3 mole., 11·5 g.) was added in small quantities, with good shaking so that the temperature did not rise above 50°; it was then left overnight, when a yellow mass separated, which was poured on to crushed ice and hydrochloric acid. The product separated as a white amorphous solid from benzene (6 g.), m.p. 195–97° (Found: N, 6·9. $C_{29}H_{17}O_{13}N_3$ requires N, 6·8 per cent.).

3-p-*Nitrobenzoyl*-4′-*Nitro*-5: 7-*dihydroxyflavone* (*V*)

The ester, on rearrangement with potassium carbonate (6 g.) and toluene, gave a cream coloured compound (4·5 g.), m.p. 272–73°, which was very insoluble in organic solvents and could not be crystallised. It is insoluble in aqueous alkali in the cold. On warming with two per cent. sodium hydroxide or by treatment with concentrated sulphuric acid in the cold, it gave 3-(*p*-nitro) benzoyl-4′-nitro-5:7-dihydroxyflavone, which crystallised from alcohol in light yellow needles, m.p. 279° (Found: N, 6·1. $C_{22}H_{12}O_9N_2$ requires N, 6·25%). Its alcoholic solution gives a violet colour with ferric chloride.

The 3-benzoyl group could not be removed; when treated with hydriodic acid in acetic anhydride, it remained unaffected and when treated with 10 per cent. alcoholic or 10 per cent. aqueous alkali, and acidified, an orange compound which did not melt was obtained.

2-p-*Nitrobenzoyl*-4: 6-*dimethyl phloracetophenone*

Phloracetophenone-4: 6-dimethyl ether was prepared by the method of Seshadri and Rao.[29] Its *p*-nitrobenzoate, prepared in the usual manner from the dimethyl ether of phloracetophenone (2·5 g.) and *p*-nitrobenzoyl chloride (2·5 g.) in pyridine, crystallised from alcohol in colourless needles (3 g.), m.p. 152–53° (Found: N, 4·3. $C_{17}H_{15}O_7N$ requires N, 4·1%).

2-*Hydroxy*-4: 6-*dimethoxy*-4′-*nitrodibenzoylmethane*

The ester (2 g.) was dissolved in benzene or toluene (30 c.c.) sodamide (2 g.) added, and refluxed for two hours. The deep red compound that separated was filtered, washed with benzene, and acidified with dilute acetic acid, the diketone collected and crystallised from acetic acid (40 c.c.) in bunches of small thin yellow needles (0·4 g.), m.p. 220–22° (Found: N, 4·2. $C_{17}H_{15}O_7N$ requires N, 4·1%).

4′-*Nitro*-5: 7-*dimethoxyflavone* (*VI*, $R = NO_2$)

The flavone, obtained by treating the diketone (0·6 g.) with concentrated sulphuric acid in the cold crystallised from acetic acid in light yellow, long

thin plates (0·4 g.), m.p. 262° (Found: N, 4·3. $C_{17}H_{13}O_6N$ requires N, 4·3%). The flavone also crystallised as yellow needles, m.p. 235° (Found: N, 4·5. $C_{17}H_{13}O_6N$ requires N, 4·3%). Crystallised again from acetic acid, the first fraction had m.p. 235°, but on dilution the filtrate gave a light yellow crystalline precipitate, m.p. 262°. Both these dimorphic forms on reduction gave the same amine.

4′-Hydroxy-5 : 7-dimethoxyflavone (VI, R = OH)

The amine, obtained by the reduction of the nitroflavone (0·5 g.) with acetic acid and iron, crystallised from alcohol in shining yellow needles (0·30 g.), m.p. 212°. Its alcoholic solution exhibits a blue fluorescence (Found: N, 4·5. $C_{17}H_{17}O_4N$ requires N, 4·7%).

4′-Hydroxy-5 :7-dimethoxyflavone, obtained by diazotisation and hydrolysis of the amine (0·3 g.) with boiling thirty per cent. sulphuric acid, crystallised from alcohol in long, light yellow needles (0·2 g.), m.p. 294–95° (Mahal and Venkataraman[9], m.p. 298°) (Found: C, 68·2; H, 4·8. $C_{17}H_{14}O_5$ requires C, 68·4; H, 4·7%). Its alcoholic solution exhibits a very weak blue fluorescence.

The *acetate* prepared by boiling with acetic anhydride and pyridine crystallised from alcohol in colourless needles, m.p. 220° (Mahal and Venkataraman,[9] m.p. 220°) (Found: C, 67·4; H, 4·7. $C_{19}H_{16}O_6$ requires C, 67·1; H, 4·7%).

4 : 5-Dihydroxy-7-methoxyflavone (Genkwanin) (IV)

The above methyl ether (0·2 g.), aluminium chloride (0·4 g.) and nitrobenzene (4 c.c.) were heated on the water-bath for one hour, ice and hydrochloric acid added, and nitrobenzene steam distilled; the yellow residue crystallised from alcohol in bright yellow needles (0·13 g.), m.p. 284–85° not depressed when admixed with a genuine sample of puddumetin (Tseng[28], m.p. 285°, Mahal and Venkataraman,[9] m.p. 285–86°) (Found: C, 67·4; H, 4·2. $C_{16}H_{12}O_5$ requires C, 67·5; H, 4·2%). It gives a brownish violet colour with ferric chloride.

The *diacetate* obtained by refluxing with acetic anhydride and pyridine crystallised from alcohol in long thin colourless needles, m.p. 197–98° (Tseng,[29] m.p. 196°; Mahal and Venkataraman,[9] m.p. 197–98°) (Found: C, 65·2; H, 4·3. $C_{20}H_{16}O_7$ requires C, 65·2; H, 4·3%).

We are greatly indebted to Dr. D. Chakravarti of Calcutta University for a sample of puddumetin and to Mr. T. S. Gore for carrying out the microanalyses.

Summary

Hydroxyflavone can be prepared from nitroflavone by reduction, diazotisation and hydrolysis. The utility of this general procedure has been shown by the synthesis of 4′-hydroxy-α-naphthaflavone, 7:4′-dihydroxy-flavone, 4′-hydroxy-7-methoxy-flavone and 5:4′-dihydroxy-7-methoxy-flavone (genkwanin). Puddumetin, isolated from *Prunus puddum*, has been proved to be identical with genkwanin.

References

1. Heap and Robinson .. *J. C. S.*, 1926, 2356.
2. ———— .. *Ibid.*, 1929, 68.
3. Lovecy, Robinson and Sugasawa *Ibid.*, 1930, 817.
4. Gulati and Venkataraman *Ibid.*, 1933, 942.
5. Seshadri and Rao .. *Ibid.*, 1946, 771.
6. Bharadwaj and Venkataraman *Curr. Sci.*, 1933, **2**, 50.
7. Nakazawa .. *Chemical Abstract*, 1940, **34**, 1017.
8. Mahal and Venkataraman *J. C. S.*, 1936, 569.
9. Shah, Mehta and Wheeler *Ibid.*, 1938, 1555.
10. Gulati and Venktaraman .. *Ibid.*, 1936, 267.
11. Baker, Brown and Scott .. *Ibid.*, 1939, 1922.
12. Shah, Virkar and Venkataraman *J. I. C. S.*, 1942, **19**, 136.
13. Seshadri and Venkateswarlu *Proc. Ind. Acad. Sci.*, 1946, **24**, 349.
14. Perkin .. *J. C. S.*, 1895, **67**, 933; 1898, **73**, 666; 1896, **69**, 1439; 1897, **71**, 186.
15. Mahal and Venkataraman *Curr. Sci.*, 1938, **6**, 450.
16. Iyer and Venkataraman .. *Proc. Ind. Acad. Sci.*, 1946, **23**, 278.
17. Bogert .. *J. A. C. S.*, 1919, **41**, 83.
18. Sugasawa .. *Chemical Abstracts*, 1938, 5833.
19. Virkar .. *J. Univ. of Bombay*, 1942, 136.
20. Baker .. *J. C. S.*, 1933, 1381.
21. Ullal, Shah and Wheeler .. *Ibid.*, 1940, 1499.
22. Virkar and Wheeler .. *Ibid.*, 1939, 1679.
23. Mahal and Venkataraman *Curr. Sci.*, 1933, **2**, 214.
24. Chakravarti and Ghosh .. *Science and Culture*, 1942–43, **8**, 463.
25. Venkataraman .. *Ibid.*, 1943–44, **9**, 45.
26. Kostanecki .. *Ber.*, 1899, **32**, 1037.
27. Mahal and Venkataraman *J. C. S.*, 1935, 866.
28. Kostanecki and Osius .. *Ber.*, 1899, **32**, 325.
29. Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, 1946, **23**, 266.
30. Tseng .. *J. Pharm. Soc. Japan*, 1935, **No. 636**, 30.

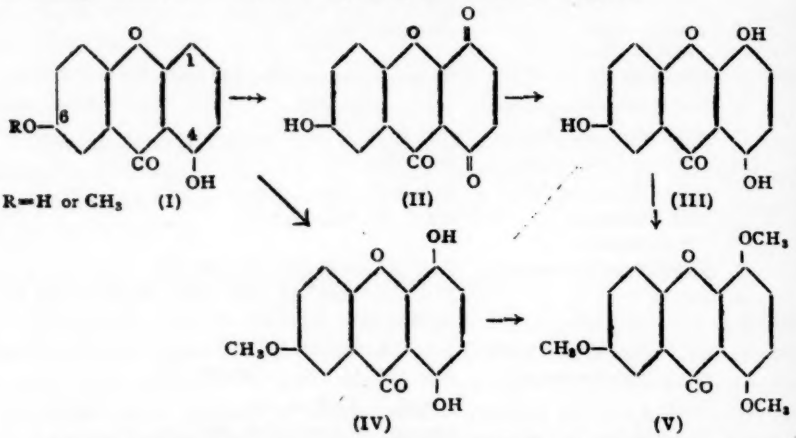
NUCLEAR OXIDATION OF EUXANTHONE

By K. Visweswara Rao and T. R. Seshadri, F.A.Sc.

(From the Department of Chemistry, Andhra University, Waltair)

Received July 15, 1947

Along with quercetin and chrysin, Nierenstein carried out the nuclear oxidation of euxanthone[1] (I, R = H) also using chromic acid in acetic acid solution. The immediate product was a quinone which could be reduced to a quinol and they were given the constitutions (II and III). Since in the other two cases[2] his results have been found to be wrong, verification of this example also has now been taken up. For this purpose the method of oxidation with persulphate which has been proved to be quite reliable in a large number of cases of hydroxy-flavones[2] is adopted.



Experiments employing euxanthone itself for the oxidation have not been successful; another reaction seems to be taking place predominantly and the yield of the required oxidation product is found to be extremely poor. However the monomethyl ether of euxanthone[3] (I, R = CH_3) could be oxidised readily to a compound having all the properties of a quinol and hence it should be given the constitution (IV). On methylation it yields the trimethyl ether (V) and on demethylation the trihydroxy compound (III) which is now named 1-hydroxy-euxanthone. During the demethylation with hydriodic acid there is a possibility of isomerisation to 3: 4: 6-trihydroxy-xanthone, as found in the case of 5: 8 and 5: 7: 8-methoxy-flavones.[4] But no such change appears to take place here since on

remethylating the trihydroxy-compound the trimethyl ether is found to be identical with the product of direct methylation of (IV).

The properties of the compounds obtained in the course of the present work are summed up in the following table and are compared with those recorded by Nierenstein. They do not agree and hence his claim is again not supported. 1-Hydroxy-euxanthone differs markedly from its isomer, gentisein particularly with regard to the colour of the substance and its reactions with sodium hydroxide and *p*-benzoquinone.

	Nierenstein's data	Present data
Trihydroxy- xanthone ..	Pale yellow needles, M.P. 328–30°	Orange yellow rectangular prisms, M.P. 300–02°
Triacetyl-derivative ..	M.P. 226–30°	188–90°
Trimethyl-ether ..	M.P. 194–95°	158–60°

Experimental

Monomethyl-euxanthone[3].—This is more conveniently prepared in the following manner.

A solution of euxanthone (1·5 g.) in anhydrous acetone (50 c.c.) was treated with dimethyl sulphate (0·7 c.c.) and freshly ignited potassium carbonate (5 g.). After refluxing for 6 hours the solvent was distilled off, the residue treated with water and the yellowish brown solid which was formed was filtered, washed with water and purified by crystallisation from alcohol. It came out in the form of glistening pale yellow plates melting at 129–30°. Yield 1 g.

6-*Methoxy*-1 : 4-*dihydroxy-xanthone* (*IV*).—

The above monomethyl-euxanthone (1 g.) was dissolved in a mixture of pyridine (20 c.c.) and aqueous potassium hydroxide (1·8 g. in 25 c.c.) and the clear yellow solution was stirred and treated dropwise with a solution of potassium persulphate (2 g. in 75 c.c.) during the course of two hours. The deep greenish brown solution was allowed to stand for 24 hours and just acidified when the unchanged methyl ether was precipitated. It was filtered off, washed and the filtrate extracted twice with ether. The clear brown aqueous solution was treated with sodium sulphite (2 g.) and concentrated hydrochloric acid (25 c.c.) and heated in a boiling water-bath for 30 minutes. The glistening yellow crystalline solid that separated out was filtered after cooling and washed with water. Some more of the product could be obtained from the filtrate by extracting with ether. Yield 0·4 g. It crystallised from ethyl acetate in the form of golden yellow long rectangular

plates melting at 280–82° with decomposition. (Found: C, 64·7; H, 3·4; $C_{14}H_{10}O_6$ requires C, 65·1; H, 3·7%.) It was sparingly soluble in alcohol, ethyl acetate and acetone. The alcoholic solution gave a deep brown colour with ferric chloride and brown-red with *p*-benzoquinone. It readily dissolved in aqueous sodium hydroxide (5%) to a deep reddish violet coloured solution.

1 : 4 : 6-*Trimethoxy-xanthone* (*V*).—

The above dihydroxy compound (0·1 g.) was dissolved in anhydrous acetone (20 c.c.) and the solution treated with dimethyl sulphate (0·3 c.c.) and anhydrous potassium carbonate (3 g.). After refluxing for 6 hours the solvent was distilled off. Water was added to the residue and the colourless solid left behind was filtered, washed and crystallised successively from a mixture of benzene and petroleum ether and from alcohol. It came out in the form of colourless narrow rectangular plates and flat needles melting at 158–60°. (Found: C, 67·5; H, 4·7; $C_{16}H_{14}O_5$ requires C, 67·1; H, 4·9%). It was sparingly soluble in ether and easily in alcohol and benzene. It was insoluble in aqueous sodium hydroxide and did not give any colour with alcoholic ferric chloride. In concentrated sulphuric acid it dissolved producing a deep red colour.

1 : 4 : 6-*Trihydroxy-xanthone* (*III*).—

The dihydroxy compound (IV) (0·2 g.) was dissolved in acetic anhydride (3 c.c.) and treated with hydriodic acid (6 c.c.) slowly with cooling. The deep reddish brown solution was gently refluxed for 1 hour, cooled, diluted with water and the free iodine present was removed by the addition of sufficient sodium sulphite. The orange coloured product was filtered, washed well with water and purified by crystallising from a mixture of ethyl acetate and benzene. It separated out in the form of orange yellow aggregates of short rectangular prisms melting at 300–02°. (Found: C, 63·6; H, 3·3; $C_{13}H_8O_5$ requires C, 63·9; H, 3·3%.) It was readily soluble in alcohol, acetone and ethyl-acetate and sparingly in ether. In alcoholic solution it gave a brown colour with ferric chloride and brown-red with *p*-benzoquinone. In 5% aqueous sodium hydroxide the solution had a deep blood-red colour. It dissolved in concentrated sulphuric acid giving a red solution.

The above trihydroxy compound (0·1 g.) was acetylated using acetic anhydride (3 c.c.) and a drop of pyridine. The acetate crystallised from alcohol in the form of colourless needles melting at 188–90°.

The trihydroxy compound (0·1 g.) was methylated in anhydrous acetone solution (20 c.c.) with dimethyl sulphate (0·5 c.c.) and potassium carbonate

(5 g.). The methyl ether crystallised from alcohol in the form of colourless narrow rectangular plates melting at 158–60 alone or in admixture with the methylation product of 6-methoxy-1 : 4-dihydroxy-xanthone.

Summary

The 6-methyl ether of euxanthone has been oxidised to 6-methoxy-1 : 4-dihydroxy-xanthone by means of alkaline persulphate. By demethylation with hydriodic acid 1 : 4 : 6-trihydroxy-xanthone has been obtained. This compound and its derivatives differ from those obtained by Nierenstein by the oxidation of euxanthone itself with chromic acid and subsequent reduction.

References

1. Nierenstein .. *Ber.*, 1913, **46**, 648.
2. Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, A, 1947, **25**, 417, 427, 432 and 444.
3. Perkin and Everest .. *Natural Organic Colouring Matters*, 1918, p. 130.
4. Baker .. *J. C. S.*, 1939, 1922.
   Shah, Mehta and Wheeler .. *Ibid.*, 1938, 1555.
   Wessely, *et al.* .. *Monatsh*, 1930, **56**, 97; 1932, **60**, 26.

CONSTITUTION OF GOSSYPIN

Part III. Ethylation of Gossypin and Conversion into Ethyl-tambuletin

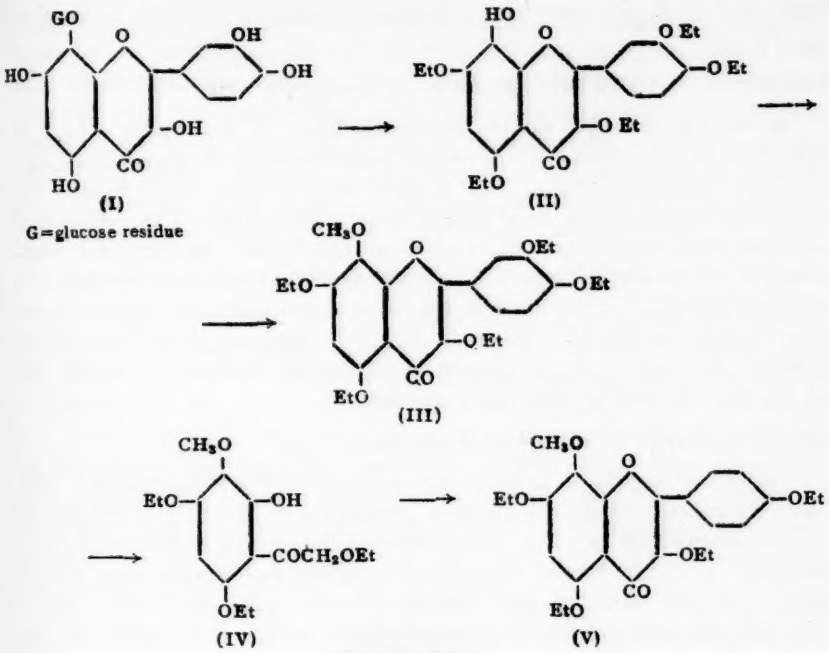
By K. Visweswara Rao and T. R. Seshadri, F.A.Sc.

(From the Department of Chemistry, Andhra University, Waltair)

Received July 15, 1947

Ethylation of hydroxyl groups does not appear to have been used as freely as methylation in the investigation of the structure of organic compounds. In several cases it is especially useful and brings about considerable simplification. As recent examples may be quoted the study of the naturally occurring partial methyl ethers of flavonols, patuletin,[1] calycopterin,[2] oroxylin-A[3] and tambuletin[4] and also of those obtained from the degradation of gossypin,[5] cannabiscitrin[6] and populnin.[7] Its applicability to the glucosides themselves appeared to merit attention particularly since the ethylation products could be correlated with those obtained from the partial methyl ethers. A few glucosides of flavonols have now been examined in this connection. Ethyl iodide has been used successfully in the past for the ethylation of the free flavonols and the partial methyl ethers. But it is not found to be suitable for the glycosides probably because of its poor activity. Diethyl-sulphate has therefore been employed and it works very satisfactorily. The ethylation of gossypin[5] is described here as a typical example.

Gossypin (I) undergoes ethylation readily by means of diethyl sulphate and anhydrous potassium carbonate in dry acetone medium and the product yields on hydrolysis a pentaethyl-ether of gossypetin (II) with a free hydroxyl group. It resembles the corresponding pentamethyl-ether[5] in its properties. When it is methylated, a compound (III) is obtained with a methoxyl in the place of the glucosidoxy group the other hydroxyl groups being ethylated. This compound is useful since it can be converted into tetra-ethyl tambuletin (V) thus confirming the relationship between gossypin and tambuletin, the former being the 8-glucoside of gossypetin and the latter the 8-methyl ether of herbacetin. For this purpose compound (III) is subjected to fission with alcoholic potash whereby O-diethyl-protocatechuic acid and gossypetol-triethyl-monomethyl-ether (IV) are obtained. The ketone (IV) is then condensed with the anhydride and sodium salt of *p*-ethoxy-benzoic acid. The transformations are represented below:



EXPERIMENTAL

O-Pentaethyl-gossypetin (II).—

Finely powdered gossypin (2 g.) was suspended in anhydrous acetone (100 c.c.) and treated with diethyl sulphate (10 c.c.) and potassium carbonate (25 g.). The mixture was refluxed for 48 hours, filtered and the potassium salts thoroughly washed with hot acetone. The filtrate was distilled to recover the solvent and the reddish brown oily liquid left behind was refluxed for 2 hours with dilute sulphuric acid (7%). On cooling the deep red solution a brown solid was obtained which was filtered off and washed with water. Yield 1 g. Crystallisation from alcohol gave pale yellow stout rectangular prisms melting at 145–47°. (Found: C, 63·7; H, 6·4; $C_{25}H_{30}O_8$, H_2O requires C, 63·2; H, 6·7%.) It was readily soluble in alcohol and the solution gave only a pale brown colour with ferric chloride. In dilute aqueous sodium hydroxide it readily dissolved to a yellow solution but in stronger alkaline solutions the solid assumed an orange colour and remained undissolved due to the formation of a sparingly soluble salt.

The above hydroxy compound (0·1 g.) was acetylated using acetic anhydride (3 c.c.) and a few drops of pyridine. The acetate crystallised

from alcohol in the form of colourless rectangular prisms melting at 147–48°.

8-Methyl-3 : 5 : 7 : 3′ : 4′-pentaethyl-ether of gossypetin (III).—

A solution of the above pentaethyl-ether of gossypetin (1 g.) in anhydrous acetone (30 c.c.) was treated with dimethyl sulphate (1 c.c.) and potassium carbonate (5 g.). The mixture was refluxed for 6 hours, the solvent was distilled off and the residue treated with water. The undissolved colourless solid was filtered off, washed with water and purified by crystallising first from alcohol and subsequently from a mixture of benzene and petroleum ether. It crystallised in the form of colourless broad rectangular plates melting at 140–42°. (Found: C, 66·2; H, 6·4; $C_{26}H_{32}O_8$ requires C, 66·1; H, 6·8%.) It was insoluble in aqueous sodium hydroxide and did not give any colour with ferric chloride.

Alkaline hydrolysis of methyl-ethyl-gossypetin (III).—

The above sample of methyl-ethyl-gossypetin (1 g.) was refluxed with absolute alcoholic potash (30 c.c. of 8% solution) for 6 hours. The solvent was then distilled off as much as possible and the residue treated with water (100 c.c.). The clear brown solution was acidified with concentrated hydrochloric acid and saturated with sodium chloride. The colourless crystalline solid that separated out was filtered and washed with a little water. It was treated with saturated aqueous sodium bicarbonate, filtered and washed with water. The filtrate (F) was preserved for the examination of the acid. The residue was dried and crystallised from a mixture of benzene and petroleum ether when the ketone (IV) separated out as colourless broad rectangular plates melting at 125–26°. (Found: C, 60·2; H, 7·5; $C_{15}H_{22}O_6$ requires C, 60·4; H, 7·4%.) It was readily soluble in alcohol and benzene and sparingly in ether and petroleum-ether. In alcoholic solution it gave a reddish violet colour with ferric chloride.

The bicarbonate filtrate (F) was acidified when a white crystalline solid separated out. It was filtered, washed with water and crystallised from aqueous alcohol. It came out in the form of colourless long rectangular rods melting at 167–68° alone or in admixture with an authentic sample of the diethyl-ether of protocatechuic acid.

p-Ethoxy-benzoic anhydride.—

A solution of *p*-ethoxy-benzoic acid (5 g.) in a mixture of anhydrous pyridine (15 c.c.) and anhydrous ether (100 c.c.) was cooled to 0° and treated with thionyl chloride (2 c.c.) in small quantities. After keeping in the ice-chest for 3 hours with occasional stirring the reaction mixture was stirred

with crushed ice and ice-cold hydrochloric acid. The colourless solid that separated out was filtered off. On distilling off the ether in the filtrate some more of the material was obtained. The total quantity was successively triturated with cold hydrochloric acid and cold sodium carbonate solution, filtered, washed with water and dried over concentrated sulphuric acid in a vacuum desiccator. Yield 4 g. Crystallisation of the product from benzene yielded colourless broad hexagonal plates melting at 110–12°. (Found: C, 68·5; H, 5·7; $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·7%.)

8-*Methoxy*-3: 5: 7: 4′-*tetraethoxy-flavone*: (O-*tetraethyl tambuletin V*).—

An intimate mixture of the ketone (IV) (0·4 g.), *p*-ethoxy-benzoic anhydride (1 g.) and sodium *p*-ethoxy benzoate (0·8 g.) was heated under reduced pressure at 170–80° for 3 hours. The reaction product was cooled and refluxed for 10 minutes with 10% alcoholic potash (30 c.c.). The solvent was distilled off under reduced pressure, the residue treated with water and the whole extracted twice with ether. On distilling off the ether a crystalline solid was obtained which was purified by crystallisation from a mixture of ether and petroleum-ether whereby it separated out as colourless rectangular plates melting at 110–12°. Mixed melting point with the tetraethyl-ether obtained from tambuletin[4] was not depressed.

Summary

Gossypin has been ethylated and hydrolysed. The resulting penta-ethyl ether of gossypetin is further methylated and the product converted into tetra-ethyl tambuletin by alkali fission and condensation of the ketonic product with the anhydride and sodium salt of *p*-ethoxy benzoic acid. This confirms the relationship between gossypin and tambuletin.

References

1. Row and Seshadri .. *Proc. Ind. Acad. Sci.*, A, 1946, **23**, 140.
2. Seshadri and Venkateswarlu *Ibid.*, 1946, **23**, 209.
3. Sastri and Seshadri .. *Curr. Sci.*, 1946, **15**, 235.
4. Balakrishna and Seshadri .. *Proc. Ind. Acad. Sci.*, A, 1947, **26**, 72.
5. Rao and Seshadri .. *Ibid.*, 1947, **25**, 397.
6. Seshadri and Venkateswarlu *Ibid.*, 1946, **23**, 29.
7. Rao and Seshadri .. *Ibid.*, 1946, **24**, 456.

COLOURING MATTER OF TAMBUL SEEDS

Part V. Synthesis of 7: 8: 4′-O-trimethyl-herbacetin considered to be identical with tambulin

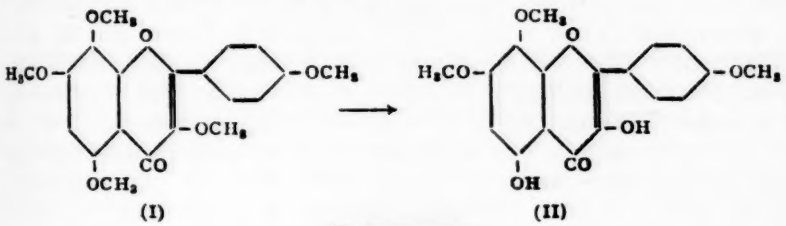
By K. J. Balakrishna and T. R. Seshadri, F.A.Sc.
(From the Department of Chemistry, Andhra University, Waltair)

Received August 14, 1947

Bose and Bose[1] who isolated tambulin from tambul seeds proposed for it the constitution of 3: 8: 4′-O-trimethyl-herbacetin. A substance of this constitution could be synthesised easily using the method of nuclear oxidation in flavones; its properties were described by Balakrishna and Seshadri in Part III.[2] It differed from tambulin markedly; its melting point was much higher and its colour less bright. It was felt that the melting point of tambulin was too low for the proposed structure. No sample of tambulin was available for further examination. However, an analysis of the evidences adduced by Bose and Bose suggested other possibilities. The isolation of anisic acid as a product of alkali fission fixed a methyl ether group in the 4′-position. From analogy with tambuletin and also from the colour reactions of tambulin the location of a second methoxyl in the 8-position seemed to be definite. Bose and Bose considered that the third methoxyl was in the 3-position because the compound was stable to æreal oxidation in alkaline solution. From our experience this could not be supported. It has been found that kæmpferol is considerably stable and could be separated from accompanying herbacetin by using this property.[3] Galangin is similarly stable. Instability does not seem to depend only on the presence of a 3-hydroxyl group, but also on the number and location of other hydroxyl groups in the molecule. Based on this point and on the observation that tambulin is different from 3: 8: 4′-O-trimethyl-herbacetin, the alternative of 7: 8: 4′-O-trimethyl herbacetin structure was considered to be more probable. The melting point of a compound of this structure was expected to agree with that of tambulin.

Among the possible methods for the synthesis of the required 7: 8: 4′-O-trimethyl herbacetin (II) partial demethylation of the pentamethyl ether of herbacetin using anhydrous aluminium chloride in nitrobenzene solution appeared to be the most convenient. This method of simultaneous hydrolysis of 3- and 5- methoxyl groups has been adopted successfully in a number of analogous cases and the synthesis of partial methyl ethers of galangin,

kæmpferol and quercetin reported recently.[4] The reaction proceeds smoothly with O-pentamethyl herbacetin and the product (II) is found to have all the properties given in the literature for tambulin. Though unfortunately the original sample of tambulin is not available for direct comparison and the determination of the mixed melting point and extraordinarily it could not be isolated in the course of our examination of the tambul seeds, the agreement in properties is so close that the constitution of tambulin may be considered to have been established.



EXPERIMENTAL

7-Hydroxy-5 : 8 : 3 : 4′-tetramethoxy-flavone was prepared according to the method of Goldsworthy and Robinson[5] by condensing 2 : 4-dihydroxy-ω-3 : 6-trimethoxy-acetophenone (1·0 g.) with anisic anhydride (10 g.) and sodium anisate (4·0 g.). The 7-hydroxy-compound was methylated in dry acetone solution using anhydrous potassium carbonate and dimethyl sulphate and pentamethyl herbacetin (I) (0·8 g.) melting at 156–58° was obtained.

3 : 5-*Dihydroxy*-7 : 8 : 4′-*trimethoxy flavone* (*II*)

To a solution of the pentamethyl ether of herbacetin (I) (0·8 g.) in dry nitrobenzene (8 c.c.) a suspension of anhydrous aluminium chloride (1·6 g.) in the same solvent (8 c.c.) was added. The mixture was heated at 100° over a boiling water-bath for one hour. After cooling the solution, petroleum ether was added when a greenish-black solid (aluminium chloride complex) separated out. It was filtered and washed free from nitrobenzene with more petroleum ether. It was then added in small quantities to ice-cold dilute hydrochloric acid. After setting aside for an hour, the yellow compound that separated out was filtered and washed free from acid. It was first crystallised from alcohol and then from a mixture ethyl acetate and petroleum ether and was thus obtained as bright yellow prisms melting at 204–205° (Found: C, 63·0; H, 5·0; $C_{18}H_{16}O_7$ requires C, 62·9; H, 4·7%). With alcoholic ferric chloride it gave an olive green colour and it dissolved in aqueous alkali freely to give a bright yellow solution slowly changing to brown. It gave an orange-red precipitate with alcoholic neutral lead acetate

and a red colour when an alcoholic solution of it was treated with concentrated hydrochloric acid and magnesium powder. Tambulin has been described as a deep yellow substance melting at 205°. Its colour reactions agree with those given above.

3 : 5-*Diacetoxy*-7 : 8 : 4′-*trimethoxy flavone*

The above compound (II) (0·1 g.) was treated with acetic anhydride (5 c.c.) and a few drops of pyridine. The solution was kept gently boiling for two hours and poured into water. When all the acetic anhydride had been decomposed, a colourless solid separated out. It was filtered and crystallised from ethyl acetate, when it came out as colourless rectangular rods and flat needles melting at 164–65°; tambulin acetate was recorded to melt at 160–61° (Found: C, 62·0; H, 5·0; $C_{22}H_{20}O_9$ requires C, 61·7, H, 4·7%). It did not give any colour with alcoholic ferric chloride and was insoluble in aqueous alkali.

Summary

Based on the evidences recorded in the past the constitution of tambulin is considered to be 7 : 8 : 4′-O-trimethyl-herbacetin. A substance of this constitution is synthesised by the partial demethylation of herbacetin-pentamethyl ether and is found to agree very closely with tambulin in properties. Hence its constitution is considered to have now been established.

References

1. Bose and Bose .. *J. I. C. S.*, 1939, **16**, 183.
2. Balakrishna and Seshadri .. *Proc. Ind., Acad. Sci.* A, 1947, **26**, 72.
3. Neelakantam, Rao and Seshadri *Ibid.*, 1943, **17**, 26.
4. Rao and Seshadri .. *Ibid.*, 1945, **22**, 383; *J. C. S.*, 1946, 771; 1947, 122.
5. Goldsworthy and Robinson *J. C. S.*, 1938, 56.

SOME ANALOGUES OF PHTHALEIN DYES FROM SUCCINIC AND MALEIC ACIDS

By N. V. Chalapathi Rao, T. R. Seshadri, F.A.Sc.
and V. Venkateswarlu
(From the Department of Chemistry, Andhra University, Waltair)

Received July 15, 1947

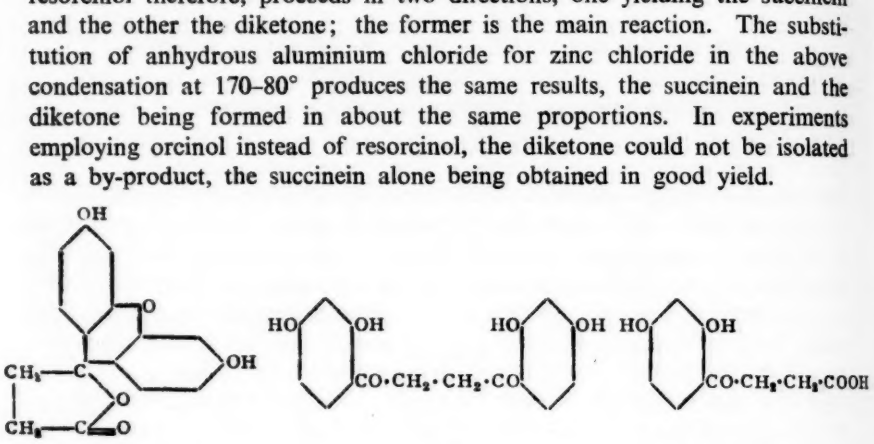
Besides their use as dyestuffs, members of the phthalein group have found other uses also. For example, tetraiodofluorescein, known as erythrosin is used as a photographic dye and also as colouring matter for foodstuffs. Tetraiodophenolphthalein has found use as a skiagraphic chemical. Considerable interest has been shown in the mercury compounds derived from these for employment as antiseptics, the most important being 'Mercurochrome'. Analogues of phthaleins derived from succinic and maleic acids have the advantage of smaller molecular weights. Consequently, higher percentages of halogens and mercury could be introduced into them. With this end in view, the preparation of succineins and maleins and their substitution products have now been investigated.

Resorcinol-succinein (I) was made earlier by Biggs and Pope[1] using succinic anhydride, resorcinol and 73% sulphuric acid and they gave its melting point as 234° (decomp.). The method does not seem to give consistent yields and, therefore, we have employed zinc chloride as the condensing agent instead, using a temperature of 170–80°. Under these conditions, it is possible to substitute succinic acid for its anhydride obtaining the same results. The succinein has been obtained in a yield of about 60% and it melts with decomposition at 254–56°.

The dibromo- and tetrabromo-derivatives of the above succinein have been reported already in the literature.[1] By modifying the method of preparation, purer products have now been prepared. Further, the tetraiodo-compound has been newly made, as also the mercuration product.

In the above preparation of resorcinol-succinein, a pale yellow by-product, insoluble in 5% hydrochloric acid (m.p. 310–12°) has been isolated in a low yield. Its composition and properties agree with the diketone constitution, 2:4:2′:4′-tetrahydroxy-dibenzoyl-ethane (II). It forms a tetra-acetate, tetramethyl and ethyl ethers, and derivatives with phenylhydrazine and dinitrophenylhydrazine. Though it dissolves in hot aqueous sodium carbonate, its acetate does not dissolve in dilute aqueous

alkali and the methyl ether is unaffected by hot aqueous alkali and cold alcoholic potash. Hence, the possibility of the product being a ketonic acid (III) is ruled out. The condensation between succinic anhydride and resorcinol therefore, proceeds in two directions, one yielding the succinein and the other the diketone; the former is the main reaction. The substitution of anhydrous aluminium chloride for zinc chloride in the above condensation at 170–80° produces the same results, the succinein and the diketone being formed in about the same proportions. In experiments employing orcinol instead of resorcinol, the diketone could not be isolated as a by-product, the succinein alone being obtained in good yield.



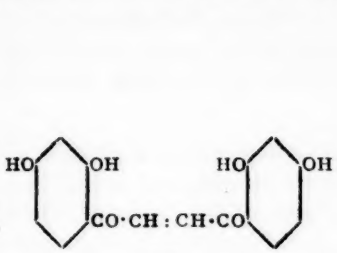
(I) (II) (III)

Von Braun *et al.*[2] have reported the formation of γ-keto-γ-2: 4-dihydroxyphenyl-*n*-butyric acid (III), m.p. 197°, in about 3% yield as a by-product by carrying out the preparation of the succinein using succinic acid, resorcinol and zinc chloride at a lower temperature, 140°.

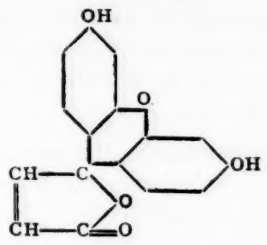
Lunge and Burckhardt[3] claimed the preparation of maleinyl-fluorescein by heating maleic anhydride with resorcinol at 150°. On recrystallisation from ether and alcohol, the product was obtained as yellowish red microscopic needles decomposing above 240° without melting. The substance was assigned the molecular formula $C_{16}H_{12}O_6$ though it contained two hydrogen and one oxygen atoms more than that required for resorcinol-malein. No other reactions of the compound were described. The crude substance was reported to give a green fluorescence in alkaline solution but nothing was said of the purified material.

On repeating their experiments, a yellowish red product was first obtained which exhibited a marked green fluorescence in alkaline solution. But it behaved as a mixture and could be separated into two fractions using difference in solubility in water. The less soluble portion consisted of a pale yellow substance melting with decomposition at 254–56° and having the molecular composition $C_{16}H_{12}O_6$, as given by Lunge and Burckhardt.[3] It exhibited very weak fluorescence in alkaline solutions and its properties

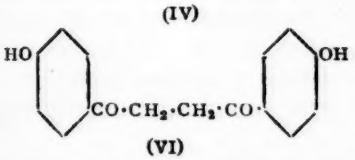
and reactions corresponded with the diketone structure, 2:4:2′:4′-tetrahydroxy-dibenzoyl-ethylene (IV). The more soluble fraction had a much deeper colour and exhibited marked fluorescence and all the properties of resorcinol-malein (V). It is, therefore, clear that in this condensation also, two products are formed, the malein in poor yield and the diketone as the major product. The malein gives the bromo-, iodo- and mercuri-derivatives. The use of zinc chloride as the condensing agent for the combination of maleic anhydride or acid and resorcinol is a disadvantage since it gives rise to resinification and the yields and purity of the products suffer.



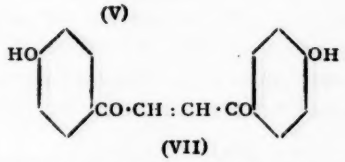
(IV)



(V)



(VI)



(VII)

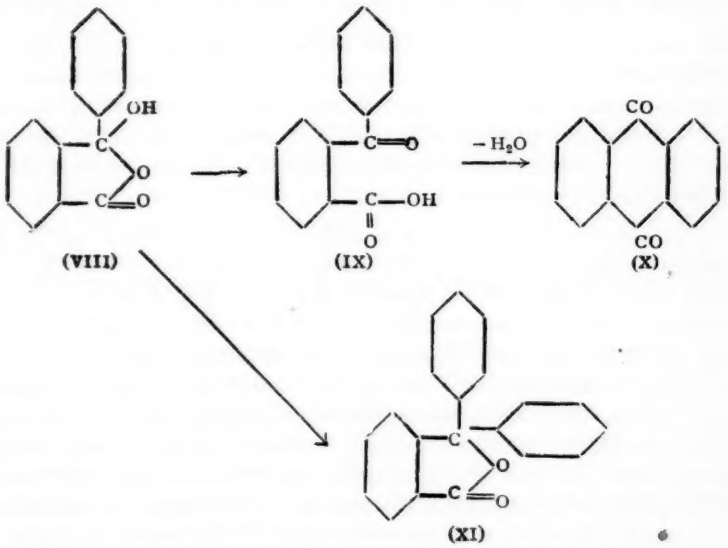
The condensation of phenol with succinic anhydride or acid does not appear to have been investigated before. The use of sulphuric acid as the condensing agent at 120° is not successful. But with zinc chloride, a small yield of a crystalline product (diketone, VI) could be obtained, the major portion being uncrystallisable resinous matter. Higher temperature, say 150°, causes more resinification.

The condensation of phenol and maleic acid was carried out by Dass and Tewari[4] in the presence of concentrated sulphuric acid at 125–35°. They described it as a brown powder blackening at 175° and melting at 195°. A repetition of the reaction showed that the yield was very poor and the product impure. By employing zinc chloride as the condensing agent, a colourless crystalline substance (m.p. 300° with decomposition) is obtained as the main product; it has the molecular composition $C_{16}H_{12}O_4$ and gives no colour with alcoholic ferric chloride indicating that the hydroxyl groups are para to the carbonyl. It does not give any prominent colour with sodium hydroxide, though the condensation product in an impure condition produces an appreciable purple colour with alkali. Obviously, the main pro-

duct is the diketone (VII) and only very minor amounts of phenol-malein are formed.

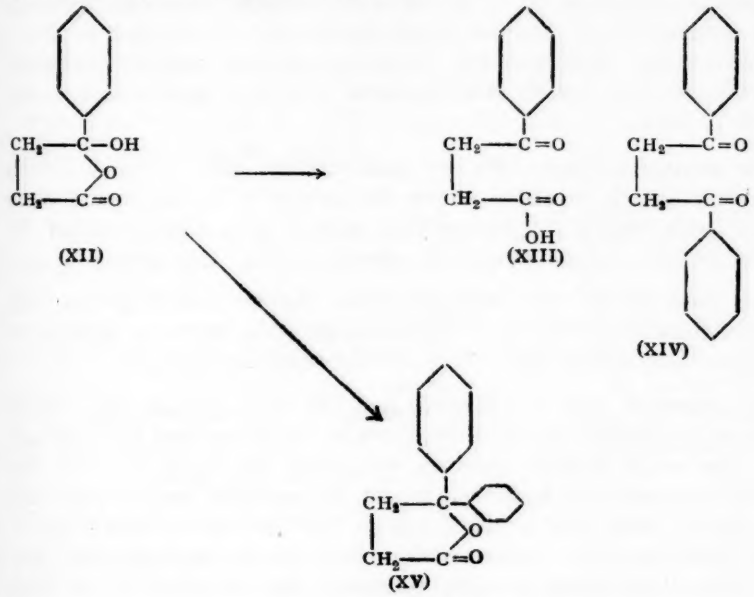
The results obtained during the course of this work could be summed up as follows. Resorcinol condenses with succinic anhydride to yield the succinein as the main product and the diketone is obtained as a small by-product. Orcinol also gives a good yield of the succinein. These could be used conveniently for the preparation of halogen and mercury substituted derivatives. The other condensations have not been successful from this point of view. Resorcinol itself gives only a poor yield of the malein, the major condensation product being the diketone. With regard to phenol, it does not give any isolable quantity of succinein or malein and only diketones could be isolated by condensations with succinic anhydride and maleic anhydride.

There seems to be a number of possible ways in which phthalic, succinic and maleic anhydrides can condense with phenols and related aromatic compounds depending upon the proportions of the reactants, condensing agent and other conditions. All these have not been realised with each substance. Representatives of several of the possible modes of combination are now available. With phthalic anhydride, the phthaleins are well known; next comes the formation of the ketonic acids as represented by benzoyl benzoic acid, and the diketone type found in the anthraquinones.



The formation of alizarin from catechol and phthalic anhydride is a well-known instance. Regarding the details of the reactions, the suggestion of von Braun,[2] *et al.*, that the initial stage involves attack of a phenol unit on one of the carbonyl groups of the anhydride as shown in (VIII) and (XII) seems to be quite acceptable. The later reactions could be represented as below.

In the case of succinic anhydride, besides the succineins (XV), the ketonic acids (XIII) and the diketones (XIV) are more easily obtained; two phenol units are involved in the formation of the diketones (XIV). Obviously, maleic acid and anhydride show little tendency to form maleins and readily yield diketones. With the aliphatic anhydrides, ring diketones of type (X) have not so far been obtained.



Experimental

Condensation of Resorcinol with succinic acid or anhydride.—

An intimate mixture of resorcinol (10·0 g.) and succinic acid (5·0 g.) was heated at 170° for ½ hour and freshly fused and powdered zinc chloride (0·5 g.) added with stirring. The heating was continued for another 3 hours, the temperature not exceeding 180°. After cooling, the reaction product was treated with acetone (25 c.c.), heated to boiling on a water-bath and

cooled; the solid product that had separated out was filtered and the residue washed with some more acetone (10 c.c.). The acetone washings were marked (W). The required succinein (A) was then separated from the residue by boiling repeatedly with 5% hydrochloric acid in which it dissolved leaving an insoluble pale yellow substance (B).

Component (A): *Resorcinol Succinein* (I).—

This was purified by crystallisation from 5% hydrochloric acid twice when it appeared as glistening dark crimson rectangular tablets with a blue reflex melting with decomposition at 254–56° (*cf.*, Biggs and Pope[1], 234°). Yield: 5·5 g. (Found: C, 56·6; H, 5·0; loss on drying *in vacuo* at 150–160° for 5 hours 15·6; $C_{16}H_{12}O_5$, $3H_2O$ requires C, 56·8; H, 5·3 and loss on drying 16·0%). It was easily soluble in acetone, sparingly soluble in alcohol, and insoluble in petroleum ether. In alkali it formed a deep red solution with a bright green fluorescence resembling that of resorcinol-phthalein. With alcoholic ferric chloride it gave a dark brown colour.

The acetone washings (W), on concentration, gave a highly viscous liquid which slowly solidified during the course of a few days. When extracted with boiling 5% hydrochloric acid it gave some more of the succinein (yield: 1·2 g.) leaving an uncrystallisable resin behind.

The same results were obtained when succinic anhydride was used instead of the acid for the above condensation. The following exploratory experiments were carried out. They are described here in brief.

(1) Resorcinol, succinic anhydride and 73% sulphuric acid were heated together at the boiling temperature according to the method of Biggs and Pope.[1] The crude product obtained was nearly theoretical in yield, but on purification using 5% hydrochloric acid, the succinein was obtained only in 20% yields. Even then it melted only at 234° and was difficult to purify further. The insoluble residue was considerable in quantity and gave strong green fluorescence in alkali solutions. But no more of the pure succinein could be extracted from it.

(2) Resorcinol, succinic acid and zinc chloride heated at 140° did not yield any appreciable amount of the succinein, the starting materials being almost completely recovered.

(3) Resorcinol, succinic acid and zinc chloride were heated together at 200°. There was considerable resinification, the yield of the succinein coming down to 10%.

(4) If instead of adding the zinc chloride to the melt of resorcinol and succinic acid kept at 170°, it was added at the laboratory temperature itself at the beginning and the reaction carried out by heating to 170–80°, the yield of the succinein was only 20% of the theoretical.

The yield of the succinein and the purity of the sample depended largely on the quality of zinc chloride that was employed and only salt of good quality should be used under the conditions described.

Tetrabromo-resorcinol-succinein.—

Resorcinol-succinein (0·5 g.) dissolved in glacial acetic acid (10 c.c.) was treated with cooling under the tap with excess of bromine in the same solvent. The solution immediately deposited a shining deep red crystalline powder. It was filtered and washed free from the mother liquor with glacial acetic acid. It appeared as rhombohedral plates under the microscope. It was sparingly soluble in glacial acetic acid and soluble in aqueous alkali, the solution giving a weak green fluorescence. It decomposed above 300° (Biggs and Pope[1], 250° d). Yield, almost quantitative. (Found: Br, 53·0; $C_{16}H_8O_5Br_4$ requires Br., 53·3%).

Dibromo-resorcinol-succinein.—

Resorcinol-succinein (0·5 g.) was dissolved in glacial acetic acid and treated with bromine (1·2 g.) in the same solvent. The solution on dilution with water precipitated the dibromo-compound. It was filtered washed with plenty of water and recrystallised from dilute acetic acid when it came out as brick-red fine needles melting with decomposition at 246–47° (Biggs and Pope[1], 237° decomp.). It was readily soluble in sodium hydroxide exhibiting a bright green fluorescence much stronger than that exhibited by the tetrabromo derivative. Yield, almost quantitative. (Found: Br, 36·5; $C_{16}H_{10}O_5Br_2$ requires Br, 36·2%).

Tetraiodo-resorcinol-succinein.—

Resorcinol-succinein (0·5 g.) was dissolved in sodium hydroxide solution (2%; 15 c.c.) and treated with a solution of iodine (2·5 g.) in aqueous potassium iodide (4·5 g. in 10 c.c. of water). The solution assumed a bright red colour and lost all its original fluorescence. Excess of iodine in the solution was then destroyed by passing sulphur dioxide through it with cooling. The solution was poured into a slight excess of ice-cold dilute hydrochloric acid. The bright red precipitate was filtered, washed with water and ground up with dilute hydrochloric acid in a mortar. It was filtered and washed repeatedly with water. The product was a deep red microcrystalline powder decomposing above 300°. It was readily soluble in

sodium hydroxide with no fluorescence. Yield, about 90%. (Found: I, 64·1; $C_{16}H_8O_5I_4$ requires I, 64·5%).

Mercuration of Resorcinol-succinein.—

Resorcinol-succinein (0·5 g.; 1 mol.) was dissolved in freshly prepared anhydrous methyl alcohol (20 c.c.) and treated with a solution of mercuric acetate (2·5 g.; about 4·5 mol.) in the same solvent (10 c.c.) containing a few drops of glacial acetic acid. Immediately, a bright red crystalline precipitate began to separate out even at the laboratory temperature. It was boiled under reflux for about 6 hours to complete the reaction and left overnight for complete precipitation. The precipitate was filtered, washed with plenty of anhydrous methyl alcohol containing glacial acetic acid to remove mercuric acetate completely. The product was finally purified by grinding with anhydrous methyl alcohol-glacial acetic acid mixture in a mortar. It was filtered and washed with anhydrous methyl alcohol. It was a deep red micro-crystalline powder decomposing above 300°. It was easily soluble in sodium hydroxide forming an orange red solution with a deep green fluorescence in dilute solutions. Yield: 2·0 g. Found: Hg, 60·7; $C_{24}H_{20}O_{13}Hg_4$ requires Hg, 60·9%).

Component (B): 2:4:2′:4′-*Tetrahydroxy-dibenzoylethane* (II).—

The orange yellow residue insoluble in 5% hydrochloric acid was boiled several times with 5% hydrochloric acid to remove traces of resorcinol-succinein and then purified by crystallisation from a large quantity of alcohol. It came out as pale yellow rhombohedral prisms melting at 310–12° and gave an intense red colour with alcoholic ferric chloride; yield, 0·2 g. (Found: C, 63·4; H, 4·8; $C_{16}H_{14}O_6$ requires C, 63·6; H, 4·6%). When dissolved in concentrated sulphuric acid, it yielded a pale yellow solution which showed a pale green fluorescence in daylight. An alcoholic solution of the substance exhibited a weak green fluorescence which increased on the addition of dilute alkali. It was soluble in sodium hydroxide and ammonia in the cold and in warm sodium carbonate and bicarbonate solutions exhibitng a feeble green fluorescence.

Methyl ether of the diketone.—The diketone (1·0 g.) was dissolved in dry acetone (50 c.c.) and boiled under reflux with dimethyl sulphate (4 c.c.) and anhydrous potassium carbonate (25 g.) for about 15 hours. The solvent was then distilled off and the residue treated with water. The separated methyl ether was crystallised from acetone when it was obtained as colourless stout rectangular plates melting at 148–50°. (Found: C, 67·1; H, 6·3 OCH_3, 34·8; $C_{20}H_{22}O_6$ requires C, 67·0; H, 6·1 and OCH_3, 34·6%). It

was unaffected by treatment with cold alcoholic potash and hence was not an ester.

Oxime of the methyl ether.—This was prepared as usual using hydroxylamine hydrochloride and sodium acetate in aqueous alcoholic solution. The product was crystallised from a large quantity of alcohol when it came out as clusters of colourless rhombohedral prisms melting at 218–20°. (Found: C, 62·1; H, 5·8; $C_{20}H_{24}O_6N_2$ requires C, 61·9; H, 6·2%).

Ethyl ether of the diketone (*II*).—The diketone (1·0 g.) was ethylated using diethyl sulphate. The ethyl ether crystallised from acetone as colourless stout prisms melting at 159–60°. (Found: C, 69·6; H, 7·0; $C_{24}H_{30}O_6$ requires C, 69·6 and H, 7·2%). It was insoluble in dilute sodium hydroxide solution.

Acetate of the diketone (*II*).—The diketone was acetylated by boiling with acetic anhydride and a few drops of pyridine for about 15 minutes. The acetate crystallised from acetone as colourless short rectangular prisms and rods melting at 140–41°. (Found: C, 61·0; H, 4·8; $C_{24}H_{22}O_{10}$ requires C, 61·3 and H, 4·7%). It was insoluble in cold dilute alkali.

The Phenylhydrazone of (*II*) was prepared by boiling a mixture of the diketone (0·5 g.), phenylhydrazine hydrochloride (1·0 g.) and sodium acetate (2 g.) in dilute alcohol. The hydrazone was crystallised from dilute alcohol when it appeared as pale red rectangular plates melting with decomposition at 208°. (Found: C, 69·4; H, 5·0; $C_{28}H_{26}O_6N_4$ requires C, 69·7; H, 5·4%).

The 2:4-*dinitrophenylhydrazone of* (*II*) was obtained by using dinitrophenyl-hydrazine hydrochloride. When crystallised from alcohol it appeared as aggregates of reddish tiny prisms melting at 185–87°. (Found: C, 51·0; H, 3·5; $C_{28}H_{22}O_{12}N_8$ requires C, 50·8; H, 3·3%).

Orcinol-succinein.—

Succinic acid (5·0 g.) and anhydrous orcinol (10·0 g.) were intimately mixed and heated at 170° for ½ hour and freshly fused zinc chloride (0·5 g.) then added with stirring. The reaction mixture was heated for another 3 hours, the temperature being maintained between 170–80°. After cooling it was treated with sodium hydroxide (100 c.c.; 2%) and filtered. The solution was acidified with ice-cold dilute hydrochloric acid avoiding excess. The precipitated fluorescein was filtered off and recrystallised from 5% hydrochloric acid when it came out as glistening dark crimson rectangular plates melting with decomposition at 259–60°. Yield, 6·8 g. (Found: C, 58·6; H, 6·4; loss on drying in vacuo at 150–60° for 4 hours 14·4; $C_{18}H_{16}O_5$, $3H_2O$ requires C, 59·0; H, 6·0 and loss on drying 14·8%). It was easily soluble

in acetone and ethyl acetate, sparingly soluble in alcohol and insoluble in petroleum ether. In alkaline solution, it formed a deep red solution with a bright green fluorescence resembling that of resorcinol-phthalein. With alcoholic ferric chloride, it gave a dark brown colour. No by-product was obtained.

Tetrabromo-orcinol-succinein.—

Orcinol-succinein (0·5 g.) was dissolved in glacial acetic acid and brominated as in the previous case with excess of bromine in the same solvent. The tetrabromo-derivative was crystallised from glacial acetic acid when it came out in the form of deep red prisms and decomposed above 300°. Yield 1·0 g. (Found: Br, 50·8; $C_{18}H_{12}O_5Br_4$ requires Br, 51·0%). It was sparingly soluble in glacial acetic acid and other common organic solvents and readily soluble in alkaline solutions with a weak green fluorescence.

Mercuration of orcinol-succinein.—

Orcinol-succinein was mercurated using mercuric acetate as described under resorcinol-succinein. It was obtained as a deep red microscopic crystalline powder decomposing above 300°. [Found: Hg, 59·4; $C_{18}H_{12}O_5$ $(Hg.O.CO.CH_3)_4$ requires Hg, 59·6%].

Condensation of maleic anhydride and resorcinol: Isolation of resorcinol malein (V) and 2:4:2′:4′-tetrahydroxy-dibenzoyl-ethylene (IV):—

Maleic anhydride (50 g.) and resorcinol (100 g.) were heated together at 150° for 2 hours. The reaction product was cooled and treated with water (300 c.c.) and stirred when a pale orange yellow precipitate (A) separated out from the dark red solution. It was filtered and washed with a small quantity of water. On concentrating the filtrate (B) and allowing it to stand, the malein (V) separated out as a crystalline solid melting at 250°. It crystallised from water as orange yellow rectangular prisms and rods melting at 268–70°. Yield. 4 g. (Found: C, 63·7; H, 4·3; loss on drying at 120° for 3 hours 5·8%; $C_{16}H_{10}O_5$, H_2O requires C,64·0; H, 4·0 and loss on drying 6·0%). It dissolved in dilute alkali giving a bright green fluorescence. In alcoholic solution it gave a green fluorescence and this was found even in sulphuric acid solution.

The residue (A) mentioned above gave only a feeble green fluorescence in alkaline solutions. It was sparingly soluble in hot water. The purification was effected by dissolving it in acetone and adding petroleum ether to the solution when a small quantity of a coloured impurity separated out, leaving the solution clear and colourless. The clear supernatant liquid was carefully decanted and the solution concentrated when it gave a pale yellow

crystalline product. Final purification was effected by crystallisation from aqueous acetone when the diketone (IV) came out as deep yellow rhombohedral prisms melting at 254–56° with decomposition. Yield, 75 g. (Found: C, 64·2; H, 4·2; $C_{16}H_{12}O_6$ requires C, 64·0 and H, 4·0%). It was soluble in sodium hydroxide forming a yellow solution with a very weak green fluorescence and gave a strong intense red colour with alcoholic ferric chloride. In concentrated sulphuric acid, it dissolved to give a pale yellow solution with a green fluorescence.

Methyl ether of (IV).—

The above diketone was boiled with dimethyl sulphate and anhydrous potassium carbonate in acetone solution for 20 hours. The product crystallised from alcohol as colourless rectangular plates melting at 139–41.° (Found: C, 67·2; H, 5·9; OCH_3, 35·0; $C_{20}H_{20}O_6$ requires C, 67·4; H, 5·6; and OCH_3, 34·8%).

Phenylhydrazone of (IV).—

This was prepared as usual using phenylhydrazine hydrochloride. The hydrazone crystallised from alcohol as bright red long rectangular plates melting at 159–60°. (Found: C, 70·2; H, 5·2; $C_{28}H_{24}O_4N_4$ requires C, 70·0 and H, 5·0%).

Dinitrophenylhydrazone of (IV).—

This was prepared as usual using 2:4-dinitrophenylhydrazine hydrochloride. The hydrazone crystallised from alcohol as bright red stout rhombohedral prisms melting at 200–202°. (Found: C, 51·1; H, 3·3; $C_{28}H_{20}O_{12}N_8$ requires C, 50·9; H, 3·0%).

Acetate of (IV).—

The diketone (1·0 g.) was gently boiled with acetic anhydride (4 c.c.) and freshly fused and powdered sodium acetate (1·0 g.) for 4 hours. After cooling it was poured into water. The product was crystallised first from acetone and finally from alcohol when it came out as colourless rectangular plates melting at 198–200°. (Found: C, 61·3; H, 4·4; $C_{24}H_{20}O_{10}$ requires C,61·5; H, 4·3%).

Tetrabromo-resorcinol-malein.—

The bromination was effected as before using excess of bromine in glacial acetic acid and resorcinol malein in the same solvent. It crystallised from glacial acetic acid as reddish brown rectangular prisms and rods decomposing above 300°. (Found: Br, 53·2; $C_{16}H_6O_5Br_4$ requires Br, 53·5%). It did not exhibit any fluorescence in alkaline solution.

Tetraiodo-resorcinol-malein.—

The iodination of resorcinol-malein was effected as described under resorcinol-succinein. The product was purified by grinding up with dilute hydrochloric acid, filtering and washing with water until it was free from acid. It was a deep reddish brown micro- crystalline powder decomposing at above 300°. (Found: I, 64·5; $C_{16}H_6O_5I_4$ requires I, 64·5%). It readily dissolved in dilute sodium hydroxide solution and emitted no fluorescence.

Mercuration of resorcinol-malein (V).—

This was effected as described under the mercuration of resorcinol succinein (I). The product was purified by grinding up with anhydrous methyl alcohol-glacial acetic acid mixture in a mortar. It was filtered and washed with anhydrous methyl alcohol. It was a deep red micro-crystalline powder decomposing above 300°. (Found: Hg, 61·0; $C_{24}H_{18}O_{13}Hg_4$ requires Hg, 61·0%). It was easily soluble in sodium hydroxide forming an orange red solution with a deep green fluorescence.

Condensation of succinic acid or anhydride with phenol: 4:4′*-dihydroxy-dibenzoyl-ethane (VI).*—

Succinic acid or anhydride (8 g.), phenol (20 g.) and freshly fused and powdered zinc chloride (2·0 g.) were intimately mixed and heated for 4 hours at 120°. The excess of phenol was then steam distilled. After cooling, the small amount of resin that separated out was removed and as no other solid product separated out, the solution was ether extracted. On concentration of the ether solution, the diketone was obtained as a colourless crystalline solid. It was recrystallised from ether when it appeared as colourless stout rhombohedral prisms melting at 190–92°; yield, 0·5 g. (Found: C, 71·0; H, 5·3; $C_{16}H_{14}O_4$ requires C, 71·1 and H, 5·2%). It dissolved easily in aqueous alkali forming a colourless solution and did not give any colour with alcoholic ferric chloride. With sulphuric acid it formed a pale orange red solution.

Condensation of maleic anhydride with phenol: 4:4′*-dihydroxy-dibenzoyl-ethylene (VII).*—

Maleic anhydride (7·0 g.), phenol (20·0 g.) and freshly fused and powdered zinc chloride (2·0 g.) were intimately mixed and heated for 4 hours at 120°. After cooling, it was poured into water (250 c.c.) and the excess of phenol steam distilled. A brown viscous liquid separated out which solidified on keeping for 24 hours. It was filtered and crystallised from 10% aqueous alcohol or a large quantity of water when it came out in the form of colourless rectangular plates melting with decomposition at 300°. (Found:

C, 71·7; H, 4·9; $C_{16}H_{12}O_4$ requires C, 71·6 and H, 4·5%). It was highly soluble in acetone and alcohol. The product easily dissolved in sodium hydroxide without any colour and did not give any colour with alcoholic ferric chloride. Yield, 4·5 g.

The same product was also obtained by using maleic acid itself instead of its anhydride, its mixture with phenol was first heated for ½ hour before adding zinc chloride. The presence of the condensing agent was essential in both cases.

4:4′-*Dimethoxy-dibenzoyl-ethylene.*—

The above diketone was methylated using dimethyl sulphate and anhydrous potassium carbonate in acetone solution by boiling for a period of 12 hours. It was crystallised from alcohol when it came out as colourless rectangular plates and prisms melting at 109–10°. (Found: C, 72·7; H, 5·7; $C_{18}H_{16}O_4$ requires C, 73·0 and H, 5·4%). It was insoluble in sodium hydroxide solution.

Summary

Resorcinol condenses with succinic anhydride forming resorcinol-succinein as the main product and tetrahydroxy-dibenzoyl-ethane as a very minor by-product. Orcinol also gives a good yield of orcinol-succinein. These could be used conveniently for the preparation of halogen and mercury substituted derivatives. Resorcinol gives only a poor yield of the malein, the major condensation product with maleic anhydride being the diketone, tetrahydroxy-dibenzoyl-ethylene. Phenol does not give any isolable quantity of succinein or malein and only the corresponding diketones could be isolated by condensation with succinic anhydride and maleic anhydride. A number of derivatives of the diketones are described.

References

1. Biggs and Pope .. *J. C. S.*, 1923, **123**, 2934.
2. Von Braun *et al.* .. *Ber.*, 1941, **74**, 1772–83.
3. Lunge and Burckhardt .. *Ibid.*, 1884, **18** (ii), 1598.
4. Dass and Tewari .. *Proc. Ind. Acad. Sci.*, A, 1941, **13**, 68.

DIAMAGNETIC SUSCEPTIBILITIES OF MAGNESIUM AND ZINC IONS

By Mata Prasad, S. S. Dharmatti and H. V. Amin
(*Chemical Laboratories, Royal Institute of Science, Bombay*)

Received March 18, 1947

On the basis of electronic theory, and quantum and wave mechanics it has been established that the diamagnetic susceptibility of an ion is given by

$$\chi_a = -2{\cdot}83 \times 10^{10} \Sigma_n \bar{r}^2 \text{ e.m.u.}$$

Van Vleck,[1] Pauling,[2] Stoner,[3] Slater[4] and Angus[5] have deduced independently several expressions for $\Sigma_n \bar{r}^2$ and have used them to calculate the diamagnetic susceptibilities of several ions. These are known as theoretical values after their names, and differ from one another appreciably in some cases.

The experimental verification of these values has been attempted on the basis that the molecular susceptibility of a heteropolar salt is the sum of the ionic susceptibilities of the constituent ions. For this purpose a certain value of susceptibility has been assigned to one particular ion. The following are some of the values (in units of -1×10^{-6}) which have been taken as standards.

$\chi_{K^+} = 15{\cdot}5$ (Joos) [6]; $\chi_{Cl^-} = 19{\cdot}5$ (Joos)[6];
$\chi_{Cs^+} = 45{\cdot}75$ (Ikenmeyer)[6];
$\chi_{I^-} = 49{\cdot}25$ (Ikenmeyer)[6]; $\chi_{H^+} = 0$ (Reicheneder)[6];
$\chi_{Li^+} = 0{\cdot}70$ (Hoare and Brindley)[6].

Using these values or others derived from them, experimental values of the susceptibilities of several ions have been determined by different workers.

A review of the literature shows that values of the susceptibilities widely different from one another have been recorded for the same ion. Angus[7] also remarks in the Annual Report of the Chemical Society, " From such a diversity of methods a diversity of values is obtained which, at present, cannot be satisfactorily sorted out ".

Looking to the fact that, " A satisfactory table of ionic susceptibilities has a considerable value " (*cf.* Stoner), attempts have been made by some workers to arrive at a set of correct ionic susceptibilities. Amongst these, a systematic study of cadmium compounds has been made by Hollens and Spencer,[9] of thallium compounds by Trew,[10] and of compounds of bismuth

(trivalent), rubidium and thallium by Bhatnagar and co-workers.[11] In order to circumvent the arbitrariness involved in using one particular value of the susceptibility of an anion Nevgi[11a] has subtracted all the known values of the anions from the molecular susceptibilities of the salts containing the same cation and have taken the arithmetic mean of the values thus obtained as the most probable value of the cation. The same procedure has been followed by Prasad and co-workers[12, 13] in deducing the ionic susceptibilities of barium, calcium and strontium ions.

Prasad and co-workers found that the theoretical susceptibilities of calcium, strontium and barium ions calculated according to Slater's and Angus' methods are in fair agreement with the experimental values deduced from salts of inorganic acids but are less than those deduced from the salts of these cations with organic anions. Some such observations were also made by Trew[10] in the case of thallium salts.

The present work was conducted with a view to establish the general validity of the conclusions mentioned above. For this purpose the magnetic susceptibilities of magnesium and zinc salts of several inorganic and organic acids were determined. The choice of the salts of these two elements was based on the fact that they belong to the same group in the periodic table as calcium, strontium and barium, but still form a separate sub-group with cadmium and mercury.

Experimental

The susceptibilities were measured by using a modified Gouy's balance. Many changes were introduced in this balance, including a new magnet, in order to increase the sensitivity and the accuracy of the balance.

Machine drawn pyrex-glass tubes with ground glass stopper were used as the containers of substances. The substances to be investigated were used in the form of fine powders and were well pressed uniformly (upto a certain mark made on the tube) to satisfy the theoretical conditions.

At the end of each measurement the specimen tube was thoroughly cleaned with water, chromic acid solution, distilled water and absolute alcohol and finally well dried before using it for the next measurement. All the compounds studied were experimented upon in two different ways: (i) two independent readings were taken for different packings in a given tube, each of these readings being taken three times, (ii) the same procedure was repeated in another tube. KCl (Merck's A. R. quality) was used as the standard substance. The magnetic susceptibility was calculated from the usual relation.

Great stress was laid on the purity of the substances used. They were either Merck's extra pure or A.R. quality or B.D.H. A.R. quality chemicals or were prepared in the laboratory; in the latter case their purity was ascertained before use.

Results

The results obtained for Magnesium salts are given in Tables I (*a*) and I (*b*) and for Zinc salts in II (*a*) and II (*b*). In these tables column 1 gives the chemical formulæ of substances along with their analysis in the case of substances prepared in the laboratory, and column 2 gives the total number (N) of electrons in the compounds. Some of the salts investigated were hydrated, hence the values (χ_m) actually measured are those of hydrated salts. For the purpose of discussion, these values have been reduced to that of anhydrous salts (χ_{ma}) by subtracting the susceptibility for molecules of water ($\chi_{H_2O} = 12 \cdot 96$) from the molecular susceptibilities of hydrated salts. Such a procedure may not be justified, since the exact effect of water

TABLE I (*a*)

Magnesium salts of Inorganic Acids

Compounds	N	Authors' values	χ_{ma} Other workers	χ_{ma} Computed experimentally	χ_{ma} Computed theoretically
1	2	3	4	5	6
MgO ..	20	0·253 .. 10·20	10·08(15)	13·46(15)	$Mg^{+2}+0^{-2}$ 15·80 (P) 16·33 (S) 14·14 (A)
$MgCO_3$ ..	42	0·3844 .. 32·41	6·99(16) 32·10(14) 33·73(15) 27·62(17) 43·00(15)	32·3 (15) 32·4 (14) 33·5 (2)	$Mg^{+2}+(CO_3)^{-2}$ 41·15 (P) 42·78 (S) 36·79 (A)
$MgSO_4 \cdot 7H_2O$ ..	60	0·5463 134·60 43·88	41·00(14) 45·11(15) 54·18(15) 43·34(18) 43·34(18) 74·59(18) 46·58(17)	43·7 (15) 43·3 (14) 44·9 (2)	$Mg^{+2}+(SO_4)^{-2}$ 55·00 (P) 57·19 (S) 49·20 (A)
$Mg_3(PO_4)_2 \cdot 4H_2O$ ..	130	0·4987 167·0 115·16		101·1 (15) 107·3 (14)	$3Mg^{+2}+2(PO_4)^{-3}$ 113·80 (P) 118·06 (S) 101·75 (A)

TABLE I (*b*)

Magnesium salts of Organic Acids

Compounds	N	Authors' values	χ_{ma} Computed experimentally	χ_{ma} Computed theoretically
$MgC_2O_4 \cdot 2H_2O$ ..	56	0·4554	38·04(15)	$Mg^{+2}+(C_2O_4)^{-2}$
Mg Found 16·39% ..		67·59		30·90 (P)
Mg Theory 16·58% ..		41·67		30·88 (S)
				30·59 (A)
$Mg(HCOO)_2 \cdot 2H_2O$ ..	58	0·4638	43·9 (15)	$Mg^{+2}+2(HCOO)^{-1}$
Mg Found 16·16% ..		69·74	44·7 (14)	36·70 (P)
Mg Theory 16·36% ..		43·82		36·68 (S)
				36·39 (A)
$Mg(CH_2)_2(COO)_2 \cdot 3H_2O$ ..	72	0·5320	61·16(15)	$Mg^{+2}+(CH_2COO)_2^{-2}$
Mg Found 12·32% ..		103·6		54·40 (P)
Mg Theory 12·63% ..		64·72		54·38 (S)
				54·09 (A)
$Mg(CH_3COO)_2 \cdot 4H_2O$ ..	74	0·5420	67·9 (15)	$Mg^{+2}+2(CH_3COO)^{-1}$
		116·22	68·3 (14)	60·20 (P)
		64·38	67·1 (14)	60·18 (S)
				59·89 (A)
$Mg(CHOH)_2(COO)_2 \cdot 5H_2O$ ..	88	0·5049	64·84(15)	$Mg^{+2}+(CHOHCOO)_2^{-2}$
Mg Found 9·08% ..		132·5		63·60 (P)
Mg Theory 9·37% ..		67·70		63·58 (S)
				63·29 (A)
$Mg(C_6H_5COO)_2 3H_2O$ ..	138	0·5638	145·3 (15)	$Mg^{+2}+2(C_6H_5COO)^{-1}$
Mg Found 7·62% ..		180·6		134·30 (P)
Mg Theory 7·68% ..		141·72		134·28 (S)
				133·99 (A)
$Mg(C_6H_4OHCOO)_2 \cdot 4H_2O$ ..	154	0·5597	152·98(15)	$Mg^{+2}+2(C_6H_4OHCOO)^{-1}$
Mg Found 6·539% ..		207·30		143·5 (P)
Mg Theory 6·637% ..		155·46		143·48 (S)
				143·19 (A)
$Mg_3(CH_2COO \cdot COH \cdot COO \cdot CH_2COO)_2 \cdot 14H_2O$	230	0·5125	188·64(15)	$3Mg^{+2}+2(CH_2COO \cdot C \cdot OHCOO \cdot CH_2COO)^{-3}$
Mg Found 10·12% ..		360·40		166·60 (P)
Mg Theory 10·49% ..		178·96		166·54 (S)
				165·67 (A)

of hydration on the compounds is still doubtful, but for purposes of comparison it should not matter much, since the correction is of a small order. The observed values of the specific susceptibilities (χ_a), the molecular susceptibilities (χ_m), and the molecular susceptibilities of anhydrous salts (χ_{ma}), are given in the third column of the Tables one below the other in the order mentioned. Columns 4 and 5 give, respectively, the experimental values obtained by the previous workers, and those computed by summing up the

values of anions and cations obtained by the same author. Since no determinations of susceptibilities of organic compounds have been made by previous workers, column 4 has been dropped in Tables I (*b*) and II (*b*); only zinc acetate $Zn(CH_3COO)_2$ has been studied by Kido and its value has been entered in column 3 along with the authors' values. All the values of susceptibilities are expressed in this paper in units of -1×10^{-6}.

TABLE II (*a*)

Zinc salts of Inorganic Acids

Compounds	N	Authors' values	Other Workers	χ_{ma} Computed experimentally	χ_{ma} Computed theoretically
$ZnCO_3$ ..	60	0·3424 .. 42·93	42·2 (14) 47·15(17)	35·7 (15) 40·9 (14)	$Zn^{+2}+(CO_3)^{-2}$ 48·95 (P) 55·17 (S) 49·35 (A)
ZnO ..	38	0·3058 .. 24·88	21·15(15) 26·85(18) 29·46(15)	16·86(15)	$Zn^{+2}+O^{-2}$ 23·60 (P) 28·72 (S) 26·70 (A)
$ZnSO_4 \cdot 7H_2O$ ..	78	0·4967 142·8 52·08	47·23(15) 43·62(18) 61·68 18) 44·60(14) 43·58(16) 52·48(17)	47·1 (15) 51·8 (14)	$Zn^{+2}+(SO_4)^{-2}$ 62·80 (P) 69·58 (S) 61·76 (A)
$Zn_3(PO_4)_2$ ..	184	0·3663 .. 141·5	..	111·3 (15) 119·46(14)	$3Zn^{+2}+2(PO_4)^{-3}$ 137·20 (P) 155·23 (S) 139·43 (A)
$ZnSeO_3$ ..	88	0·2814 .. 54·19	..	60·3(14)	..

DISCUSSION OF RESULTS

It will be noticed from the above Tables that the χ_{ma} values of some compounds obtained by the authors agree well with those found by the previous workers. Values of χ_{ma} calculated according to the method developed by Angus and Farquharson[19] by summing up the susceptibilities of the constituent atoms in the required ionic state (*cf.* column 6) show that in many cases they are widely different from the experimental values. Similar observations were made by Prasad, Dharmatti and Gokhale.[13] However, the agreement between the experimental values and those computed by

TABLE II (*b*)

Zinc salts of Organic Acids

Compounds	N	Authors' values	χ_{ma} Computed experimentally	χ_{ma} Computed theoretically
$Zn(COO)_2 \cdot 2H_2O$ ..	74	0·4097	41·44(15)	$Zn^{+2}+(C_2O_4)^{-2}$
Zn Found 34·11% ..		77·61		38·17 (P)
Zn Theory 34·5 % ..		51·69		43·27 (S)
				43·15 (A)
$Zn(HCOO)_2 \cdot 2H_2O$ ..	76	0·4004	47·3 (15)	$Zn^{+2}+2(HCOO)^{-1}$
Zn Found 34·28% ..		..	53·2 (14)	44·5 (P)
Zn Theory 34·39% ..		50·73		49·07 (S)
				48·95 (A)
$Zn(CH_2)_2(COO)_2$ ..	90	0·4033	65·16(15)	$Zn^{+2}+(CH_2COO)_2^{-2}$
Zn Found 35·91% ..		..		62·20 (P)
Zn Theory 36·04% ..		73·14		66·77 (S)
				66·65 (A)
$Zn(CH_3COO)_2 \cdot 2H_2O$ ..	92	0·4600	71·3 (15)	$Zn^{+2}+2\ CH_3COO)^{-1}$
		100·9	74·8 (14)	68·00 (P)
		74·98		72·57 (S)
		76·8(14)		72·45 (A)
$Zn(CHOH)_2(COO)_2 \cdot 2H_2O$ ..	106	0·4244	68·24(15)	$Zn^{+2}+(CHOHCOO)_2^{-2}$
Zn Found 25·86% ..		105·9		71·40 (P)
Zn Theory 26·20% ..		79·98		75·97 (S)
				75·85 (A)
$Zn(C_6H_4 \cdot COO \cdot COO)$ ..	114	0·4204	94·64(15)	$Zn^{+2}+(C_6H_4COO \cdot COO)^{-2}$
Zn Found 28·26% ..		..		87·5 (P)
Zn Theory 28·38% ..		96·42		92·07 (S)
				91·95 (A)
$Zn(C_6H_5COO)_2$ ..	156	0·5006	148·7 (15)	$Zn^{+2}+2(C_6H_5COO)^{-1}$
Zn Found 20·92% ..		..		142·1 (P)
Zn Theory 21·25% ..		154·0		146·67 (S)
				146·55 (A)
$Zn(C_6H_4OHCOO)_2 3H_2O$ ..	172	0·5129	152·88(15)	$Zn^{+2}+2(C_6H_4OHCOO)^{-1}$
Zn Found 16·49% ..		201·90		151·30 (P)
Zn Theory 16·61% ..		163·02		155·87 (S)
				155·75 (A)
$Zn_3(CH_2 \cdot COO \cdot COH \cdot COO \cdot CH_2COO)_2 \cdot 2H_2O$	284	0·4032	188·34(15)	$3Zn^{+2}+2(CH_2 \cdot COO \cdot COH COO \cdot CH_2COO)^{-3}$
Zn Found 31·98% ..		246·10		190·00 (P)
Zn Theory 32·13% ..		220·18		203·71 (S)
				203·35 (A)

adding the cation and anion values given by the same author is fairly good (*cf.* columns 3 and 5).

(*a*) *Electronic Isomers*

Bhatnagar and co-workers[20] have empirically shown that the molecular susceptibility of a salt is given by

$$\chi_{ma} = -2{\cdot}832 \times 10^{10} \cdot \overline{r^2}^{2} \cdot K,$$

where the numerical factor K should have the same value for a set of electronic isomers. This relation can be used to calculate the value of χ_{ma} of a compound if its $\overline{r^2}$ and K of its series of isomers are known. The authors have used this relation to calculate the molecular susceptibilities of some of the compounds studied in this investigation. For this purpose the χ_{ma} values of the isomers are taken from International Critical Tables, 1929, Landolt Bornsteins Physikalische Chemischen tabellen, 1930, and from other available literature. The values of $\overline{r^2}$ have been estimated by using Bragg's theory[21] of closest packing. The values of K and χ_{ma} for some salts of Magnesium and Zinc calculated for different isomers are given in columns 6 and 7 of Table III.

TABLE III

No. of atoms	Total No. of Electrons	Electronic Isomers	χ_{ma} Observed	Radius in A. U.	K	χ_{ma} Calculated
5	42	$MgCO_3$	32·41*	1·606	..	18·67
		$NaNO_3$	25·60(18)	1·88	2·557	..
6	60	$MgSO_4$	43·88*	1·714		52·35
		$AlPO_4$	49·33	1·664	6·292	38·25
				1·946	4·598	..
5	60	$ZnCO_3$	42·13*	1·530	..	17·57
		$KClO_3$	36·81(15)	2·219	2·650	..
5	88	$ZnSeO_3$	54·19*	1·678	..	33·43
		$NaIO_3$	51·77(17)	2·088	4·192	..
2	38	ZnO	24·88*	1 97	..	20·01
		Libr	37·3(18)	2·69	1·82	..
2	20	MgO	10·2*	2·07	..	16·03
		LiCl	24·3(15)	2·55	1·32	..
6	78	$ZnSO_4$	52·08*	1·646	..	23·60
		K_2SO_3	63·70(14)	2·704	3·076	..

* Authors' values.

It is clearly seen from this Table that the values of χ_{ma} calculated from the K value of its isomer are far different from the experimental ones. Similar disagreement has been found in the case of other salts as well.[13]

(b) Graphical discussion of the results of molar susceptibilities

From the study of the halides of alkali and alkaline earth metals Ikenmeyer[23] has shown that the molecular susceptibility is a linear function of the sum of the nuclear charges of the atoms constituting the molecules and can be expressed in the form $-\chi_{ma} = C_1\Sigma Z + C_2$ where ΣZ is the sum of the electrons in the compound and C_1 and C_2 are specific constants for a given series of salts. To verify this relation values of χ_{ma} were plotted against ΣZ by Kido,[14] Trew,[10] and Prasad, Dharmatti and co-workers.[12, 13] Kido[14] found that the curves were definitely linear. Trew noticed some deviation from linearity and explained them as 'specific effects due to the crystalline forms of compounds investigated'. Prasad, Dharmatti and co-workers[12,13] not only found definite divergences from the linear relation but observed a pattern in these curves, which was repeated in the same way for the same salts of calcium, strontium and barium and thereby established the family relationship of the three elements from a new view point.

Values of χ_{ma} for the same salts of magnesium and zinc were plotted against ΣZ by the authors and the graphs marked as (*a*) and (*b*), obtained are shown in Fig. 1. The non-linearity of the graphs definitely shows that

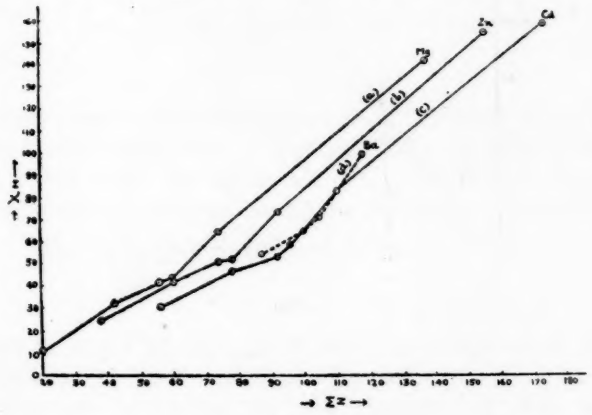


FIG. 1

Ikenmeyer's relation is not generally true and supports the observations of Prasad, Dharmatti and co-workers. The observed divergences may be due to different susceptibility contributions of the different anions.

Values of χ_{ma} have been plotted against ΣZ for the same salts of cadmium and barium as those of magnesium and zinc in Fig. 1 and are marked as (*c*) and (*d*). The values of χ_{ma} for cadmium salts were taken from Hollens

and Spencer[9] and those for barium from Prasad, Dharmatti and Kanekar.[11] It will be noticed that the plots for salts of magnesium, zinc and cadmium are of the same pattern while that of barium is definitely different. This is expected from the chemical analogy and the family characteristics of magnesium, zinc and cadmium.

When, however, the values of χ_{ma} were plotted against ΣZ separately for inorganic and organic salts of magnesium and zinc, the curves shown in Fig. 2 were obtained. These are very nearly straight lines in all the four

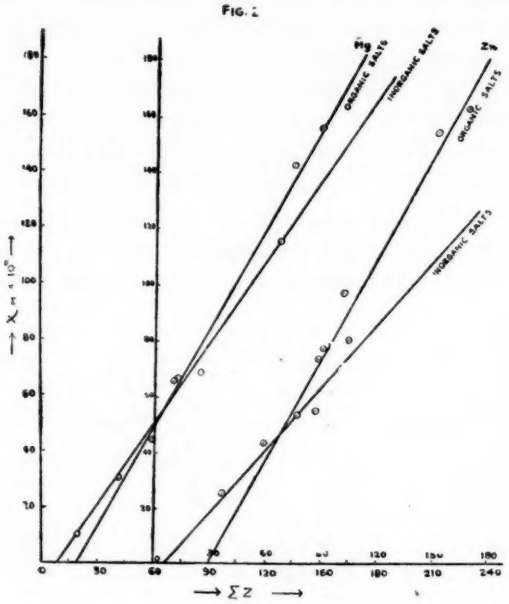


FIG. 2

cases. The linear relationship between χ_{ma} and ΣZ suggested by Ikenmeyer is therefore true in the case of magnesium and zinc compounds when the organic and the inorganic salts are considered separately. Another important feature which will be noticed in Fig. 2 is that the slopes of the lines relating to the organic compounds are higher than those for the inorganic ones, showing thereby that the contribution per electron is higher in the case of organic salts than in the inorganic ones.

Further, when the values of χ_{ma} for salts containing the same anions were plotted against the number of electrons (N) in magnesium, zinc, and cadmium ions, the graphs obtained, shown in Fig. 3, were a set of nearly

FIG 3

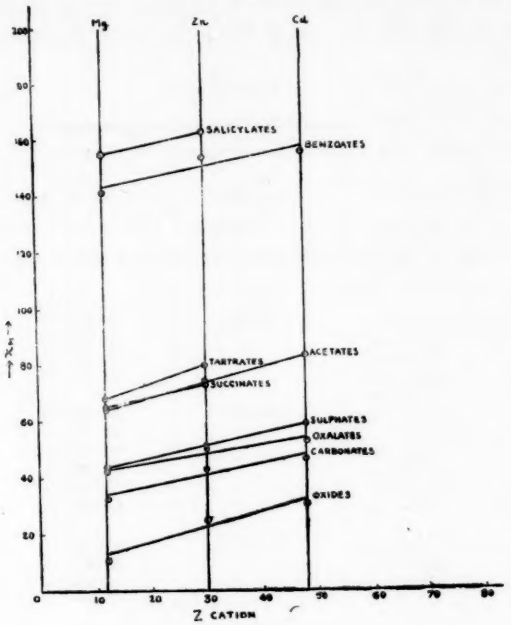


FIG. 3.

parallel straight lines. These lines have been smoothened out to some extent in the same manner as followed by Prasad, Dharmatti and Gokhale.[13] The values of C_1 and C_2 in the equation, $-\chi_{ma} = C_1N + C_2$ for these lines, have been evaluated for different anions and are given in Table IV. Although

TABLE IV

Anions	Values for the Mg–Zn–Cd Series	
	C_1	C_2
Benzoates ..	0·5286	67·65
Phosphates ..	0·4781	48·00
Acetates ..	0·5150	29·00
Sulphates ..	0·4477	38·10
Oxalates ..	0·4202	36·50
Carbonates ..	0·4469	27·00
Oxides ..	0·6138	3·00
Formates ..	0·3838	19·20
Succinates ..	0·4677	58·80
Tartrates ..	0·6829	59·20
Citrates ..	0·7633	84·90

all the values of C_1 are not the same as required by the parallelism of all the lines, yet they do not deviate much from the mean excepting in one or two cases.

TABLE V

Ionic susceptibilities of magnesium

Compound	χ_{ma} Authors	χ_{anion} Other workers	$\chi_{Mg^{++}}$
(*a*) Values Mg^{++} from magnesium salts of inorganic acids			
MgO ..	10·2	3·36(15)	6·84
$MgCO_3$ ..	32·41	22·20(15)	10·21
		28·10(14)	4·31
		24·59(17)	7·82
		29·50(10)	2·91
$MgSO_4$ ..	43·88	33·60(15)	10·28
		39·00(14)	4·88
		37·00(10)	6·88
		39·00(10)	4·88
		40·10(10)	3·78
		37·50(17)	6·38
$Mg_3(PO_4)_2$ ..	115·16	47·20(11)	6·92
		40·43(17)	11·43
		35·40(15)	14·79
		43·49*	9·39
(*b*) Values of Mg^{++} from magnesium salts of organic acids			
Magnesium formate ..	43·82	16·9*	10·02
		20·2 (14)	3·42
		17·3 (27)	9·22
		17·6 (27)	8·62
Magnesium acetate ..	64·38	28·90(15)	6·58
		32·00(14)	0·38
		30·00(10)	4·38
		30·00(9)	4·38
		29·80 27)	4·78
		31·40(14)	1·58
		30·20(27)	3·98
		28·76*	6·86
Magnessium benzoate ..	141·72	67·60*	6·52
		66·10(10)	9·52
Magnessium citrate ..	178·96	79·17*	6·87
Magnessium oxalate ..	41·67	27·94*	13·73
		28·50(9)	13·17
Magnesium salicylate ..	155·45	72·69*	10·07
Magnesium succinate ..	64·72	51·66*	13·06
Magnesium tartrate ..	67·90	63·80(10)	3·90
		60·88*	6·82

* These values are obtained by adding Pascal's corrected values for various constituents.

TABLE VI

Ionic susceptibilities of zinc ion

Compound	χ_{ma} Authors	χ_{anion} Other workers	$\chi_{Zn^{++}}$
(*a*) Values of Zn^{++} from zinc salts of inorganic acids			
ZnO ..	24·88	3·36(15)	21·52
$ZnCO_3$ ..	42·93	22·20(15)	20·73
		28·10(14)	14·83
		24·59(17)	18·34
		29·50(10)	13·43
$ZnSO_4$ ..	52·08	33·60(15)	18·48
		39·00(14)	13·08
		37·00(10)	15·08
		39·00(10)	13·08
		40·10(10)	11·98
		37·50(17)	14·58
$Zn_3(PO_4)_2$ ..	141·5	47·20(11)	15·70
		40·43(17)	20·21
		35·40(15)	23·57
		43·49*	18·17
$ZnSeO_3$ ..	54·19	44·90(27)	9·29
		47·50(14)	6·69
		39·59**	14·60
(*b*) Values of Zn^{++} from zinc salts of organic acids			
Zinc formate ..	50·73	16·9*	16·93
		20·2 (14)	10·33
		17·3 (27)	16·13
		17·6 (27)	15·53
Zinc acetate ..	74·98	28·90(15)	17·18
		32·00(14)	10·98
		30·00(10)	14·98
		30·00(9)	14·98
		29·80(27)	15·38
		31·40(14)	12·18
		30·20(27)	14·58
		28·76*	17·46
Zinc benzoate ..	154·00	67·60*	18·62
		66·10(10)	21·80
Zinc citrate ..	220·18	79·17*	20·61
Zinc oxalate ..	51·69	27·94*	23·75
		28·50(9)	23·19
Zinc salicylate ..	163·02	72·69*	17·64
Zinc succinate ..	73·14	51·66*	21·48
Zinc tartrate ..	79·98	63·80(10)	16·18
		60·88*	19·10
Zinc phthalate ..	96·42	81·14	15·28

* These values are obtained by adding Pascal's corrected values for various constituents.

** Mean value obtained from some selenites.

(*c*) *Ionic Susceptibility*

The susceptibilties of magnesium and zinc ions were deduced by subtracting all the known experimental values of anions of various other workers from the molecular susceptibilities of the salts studied in this investigation. The anion values used are given in column 3 of Tables V and VI. The values thus obtained are given in the last column of these Tables. No distinction has been made, as has been done in the previous publications from this laboratory,[13] between the solid and the solution data in evaluating the ionic susceptibilities, since the results are not much affected by such a distinction. Two separate means were taken for values of $\chi_{Mg^{++}}$ and $\chi_{Zn^{++}}$ given in the last columns of Tables V and VI, one deduced from inorganic salts and the other from the organic ones. These mean values are given in column 2 of Table VIII.

Another method was followed for the evaluation of the ionic susceptibilities of magnesium and zinc ions. Values of C_2 (Table IV), obtained by producing the smoothened straight lines shown in Fig. 3 to meet the χ_m axis were taken to be the values of the susceptibilities of the respective divalent anions. Subtracting these anion values from the molecular susceptibilities of these magnesium and zinc salts, the ionic susceptibilities of Mg^{++} and Zn^{++} were deduced from each salt. The results obtained from the inorganic and the organic salts are given under two separate heads in Table VII.

TABLE VII

Anion	χ_{anions}	$\chi_{Mg^{++}}$	$\chi_{Zn^{++}}$
(*a*) Inarganic Salts			
Oxide ..	3·00	7·20	21·88
Carbonate ..	27·00	5·41	15·93
Sulphate ..	38·10	5·78	13·98
Phosphate ..	49·50	5·39	14·17
(*b*) Organic Salts			
Oxalate ..	36·50	5·17	15·19
Acetate ..	29·00	6·38	16·98
Benzoate ..	67·65	6·42	19·70
Salicylate ..	75·00	5·46	13·02
Formate ..	19·20	5·42	12·33
Succinate ..	58·80	5·92	14·34
Tartrate ..	59·20	8·50	20·78
Citrate ..	77·00	8·32	22·06

The mean values of ionic susceptibilities deduced for magnesium and zinc ions from the inorganic and organic salts from the above Table are given in the third column of Table VIII.

TABLE VIII

Ions	χ_{ion} from Tables V & VI	χ_{ion} from Table VII
Mg^{++} Inorganic ..	7·45	5·95
Mg^{++} Organic ..	7·04	6·45
Zn^{++} Inorganic ..	15·74	16·49
Zn^{++} Organic ..	17·01	16·80

The values of susceptibilities for magnesium ion theoretically calculated according to Slater[4] and Angus[5] are 3·11 and 2·88, respectively, while those for zinc ion are 15·82 and 15·46. On comparing these values with those obtained in this investigation it is clear that the calculated values for magnesium ion are much lower than the experimental ones, while they are nearly the same as deduced from inorganic and organic salts in the case of zinc ion.

It appears from the above Table that the mean values of the susceptibilities of Magnesium and Zinc ions deduced from salts of organic acids are higher than those obtained from salts of inorganic acids, as it happens to be in the case of calcium, strontium and barium ions.[12,13] But when these results were subjected to statistical analysis, the differences between the two values were found to be insignificant. Hence these results can only have a qualitative meaning in support of the results of the aforesaid workers.[12,13]

Prasad, Dharmatti and Kanekar[12] have observed that as the number of carbon atoms in barium salts of organic acids increases, there is an increase in the susceptibility of the cation. The results obtained by Prasad, Dharmatti and Gokhale[13] also indicate the same trend. Hence the mean of all the values of $\chi_{Mg^{++}}$ and $\chi_{Zn^{++}}$ deduced from salts of different organic acids [*cf.* last column of Tables V (*b*) and VI (*b*)] were obtained and are given in the last column of Table IX which also gives the number of carbon atoms (column 2) and the total number of electrons (column 3) in the salts of the two elements.

It is clear from the results given in the above Table that the ionic susceptibility of a cation does not bear any quantitative relation with the number of carbon atoms in the anion.

TABLE IX

Compounds	No. of C atoms	No. of Electrons	Observed χ_{ma}	χ_{cation}
		(*a*) Magnesium salts		
Oxalate ..	2	56	41·67	13·45
Formate ..	2	58	43·82	7·82
Succinate ..	4	72	64·72	13·06
Acetate ..	4	74	64·38	4·11
Tartrate ..	4	88	67·7	5·36
Citrate ..	12	200	178·96	6·87
Benzoate ..	14	138	141·72	8·02
Salicylate ..	14	154	161·46	10·07
		(*b*) Zinc salts		
Oxalate ..	2	74	51·69	23·47
Formate ..	2	76	50·73	14·73
Succinate ..	4	90	73·14	21·48
Acetate ..	4	92	74·98	16·82
Tartrate ..	4	106	79·98	17·64
Phthalate ..	8	114	95·59	15·28
Citrate ..	12	284	220·18	20·61
Benzoate ..	14	156	154·00	20·21
Salicylate ..	14	172	157·02	17·64

(*d*) *Ionic Radius*

Ionic radii of magnesium and zinc ions were calculated from the susceptibilities of these ions deduced from inorganic and organic salts from the relation,

$$\sqrt{\frac{\Sigma r_e^2}{\Sigma r_t^2}} = \frac{r'_e}{r'_t}$$

where $\Sigma \bar{r}_e^2$ is computed from the known value of χ_{ion} from Langevin's equation, $\Sigma \bar{r}_t^2$ is calculated theoretically from Slater's approximate wave function, and r'_t is the effective radial electron density of the outermost shell. The calculated values of radii are given in Table X. For the sake of comparison the values of radii of magnesium and zinc ions obtained by other methods are also included in this Table.

TABLE X

Ions	Author's calculated values of ionic radius in Å. U.	Values of Ionic radius by other workers from X-ray data in Å. U.		
		Wyckoff[23]	Bragg[24]	Clark[26]
Mg^{++} (Inorganic) ..	0·9645	0·75	0·75	0·65
Mg^{++} (Organic) ..	0·9833			
Zn^{++} (Inorganic) ..	1·233	0·83	..	0·74
Zn^{++} (Organic) ..	1·263			

References

1. Van Vleck .. *Phys. Rev.*, 1928, **31**, 587.
2. Pauling .. *Proc. Roy. Soc.*, 1927, **114 A**, 181.
3. Stoner .. *Proc. Phil. Soc. Leeds*, 1929, **1**, 484; *Magnetism and Matter*, ed. 1934, p. 279.
4. Slater .. *Phys. Rev.*, 1930, **57**, 36; also Stoner's *Magnetism and Matter*, p. 279.
5. Angus .. *Proc. Roy. Soc.*, 1932, **136 A**, 569.
6. Joos .. Stoner's *Magnetism and Matter*, ed. 1934, pp. 269–71.
7. Angus .. *Annual Reports, Chem. Soc.*, 1941, **38**, 37.
8. Stoner .. *Magnetism and Matter*, 1934, p. 269.
9. Hollens and Spencer .. *J. C. S.*, 1935, 495.
10. Trew .. *Trans. Farad. Soc.*, 1936, **32**, 1658; 1941, **37**, 476.
11. Bhatnagar and co-workers *Curr. Sci.*, 1935, **4**, 153, 234; *J. Indian Chem. Soc.*, 1935, **12**: 799; 1936, **13**, 273.

11*a*. Nergi .. *J. Univ, Bom.*, 1940, **7**, 19.

12. Prasad, Dharmatti and Kanekar *Proc. Ind. Acad. Sci.*, 1942, **16**, 307.
13. ——, —— and Gokhale *Ibid.*, 1944, **20**, 224.
14. Kido .. *Science Reports, Tohoku Imp. Univ.*, 1932, **21**.
15. .. *Int. Crit. Tables*, 1929, **6**.
16. Bhatnagar and Dhawan .. *Phil. Mag.*, 1928, **5**, 536.
17. Prasad and Desai .. Unpublished work.
18. .. *Landolt Bornstein*, **4**, 1245.
19. Angus and Farquharson .. *Proc. Roy. Soc.*, 1932, **136 A**, 579.
20. Bhatnagar and R. N. Mathur *Phil. Mag.*, 1928, **6**, 217.
    —— and Luther .. *Jour. Ind. Chem. Soc.*, 1929, **6**, 303.
21. Bragg .. *Phil. Mag.*, 1920, **40**, 169.
22. B. N. Ghosh .. *Thesis* submitted to Bombay University, 1946.
23. Ikenmeyer .. *Ann. Phys.*, 1929, **1**, 167.
24. Bragg .. *Phil. Mag.*, 1926, **2**, 258.
25. Wyckoff .. *The Structure of Crystals*, 1931, p. 192.
26. Clark .. *Applied X-Rays*, p. 356.
27. Rao and Shreeraman .. *Phil. Mag.*, 1937, **24**, 1034; *Curr. Sci.*, 1937, **3**, 55.

DIAMAGNETIC SUSCEPTIBILITY OF LEAD ION

By Mata Prasad, F.A.Sc., S. S. Dharmatti and D. D. Khanolkar
(*Chemical Laboratories, Royal Institute of Science, Bombay*)

Received March 18, 1947

Previous systematic investigations on the magnetic properties of a large number of inorganic and organic compounds of Ca, Sr, Ba, Mg and Zn deal with the determination of the diamagnetic susceptibilities of these cations by the method of averages and other methods. An important result accruing from these investigations is the establishment of the fact that the mean ionic susceptibility values of cations deduced from the salts of organic acids are higher than those obtained from the salts of inorganic acids.

The ionic susceptibility of Pb given in the 'International Critical Tables' is $-46{\cdot}0 \times 10^{-6}$ (Pascal) while a mean value deduced from lead salts studied by Kido[1] comes out to be $-30{\cdot}07 \times 10^{-6}$. The values calculated according to Slater and Angus are $-50{\cdot}2 \times 10^{-6}$ and $-49{\cdot}9 \times 10^{-6}$, respectively. Hence in order to obtain an accurate experimental value of Pb^{++}, which could be compared with the theoretically calculated values without any ambiguity the molecular susceptibilities of several lead salts of inorganic and organic acids were measured by the same method and technique as followed in previous investigations. The results obtained have been utilised to examine the findings of Prasad and co-workers[2] regarding the differences in susceptibilities of cations deduced from their salts of inorganic and organic acids.

Experimental and Results

All the salts used in this investigation were chemically pure; they were either of Merck's Extra-Pure quality or were prepared in a pure state in the laboratory. The results obtained are given in column 3 of Table I. Each susceptibility value given in the Table is the mean of six closely agreeing measurements, each being the mean of three readings. Each measurement was made with a fresh packing of the substance.

In order to compare the observed values with those computed by adding the empirical values for susceptibilities of the anion and the cation given by the same investigator (column 5) the observed molar susceptibilities for the anhydrous salts were obtained by deducting the susceptibility value of water molecules ($\chi_{H_2O} = 12{\cdot}96$) from the experimental molecular susceptibilities of the hydrated salts. The experimental values obtained by previous

workers are given in column 4 of Table I (*a*). Since no determinations of susceptibilities of organic compounds have been made by previous workers, column 4 has been dropped in Table I (*b*); only lead acetate has been

TABLE I (*a*)

Lead Salts of Inorganic Acids

Compounds	N	Authors' values	χ_{ma} Other workers	χ_{ma} Computed experimentally	χ_{ma} Computed theoretically
$PbCO_3$ ..	112	0·2259 60·36 60·36	.. ..	68·2(4) 58·2(1)	$Pb^{+2}+(CO_3)^{-2}$ 89·8 (S) 83·8 (A)
$PbCl_2$ .. Pb Found =74·10% Pb Theory =74·46%	116	0·2923 .. 81·30	89·00(4) 73·48(1)	86·2(4) 74·3(1)	$Pb^{+2}+2(Cl)^{-1}$ 101·78 (S) 95·62 (A)
$PbSO_4$ ..	130	0·2420 .. 73·36	69·01(1) 77·96(5)	79·6(4) 69·1(1)	$Pb^{+2}+(SO_4)^{-2}$ 104·21 (S) 96·21 (A)
$PbCrO_4$ .. Pb found =64·10% Pb theory =64·07%	138	0·0563 .. 18·18	..	..	$Pb^{+}+(CrO_4)^{-2}$ 108·30 (S) 100·05 (A)
PbS_2O_3 .. Pb found =64·78% Pb theory =64·89%	138	0·2619 .. 83·60	..	89·4(4) 73·1(1)	$Pb^{+2}+(S_2O_3)^{-2}$ 113·91 (S) 105·63 (A)
$Pb(CNS)_2$ .. Pb found =64·02% Pb theory =64·07%	140	0·3111 .. 100·60	..	..	$Pb^{+2}+2(CNS)^{-1}$ 214·20 (S) 183·74 (A)
$Pb(NO_3)_2$ ..	144	0·2320 .. 76·85	82·15(4) 71·20(1) 77·03(5)	74·4(4) 70·3(1)	$Pb^{+2}+2(NO_3)^{-1}$ 129·32 (S) 117·62 (A)
$PbBr_2$ .. Pb found =56·51% Pb theory =56·39%	152	0·2776 .. 101·90	102·80(4)	107·4(4) 99·5(1)	$Pb^{+2}+2(Br)^{-1}$ 130·22 (S) 123·20 (A)
PbI_2 .. Pb found =44·7% Pb theory =44·89%	188	0·3019 .. 139·20	152·20(4)	135·2(4) 136·5(1)	$Pb^{+2}+2(I)^{-1}$ 169·86 (S) 160·54 (A)
$Pb(BrO_3)_2 \cdot H_2O$ Pb found =43·10% Pb theory =43·03%	200	0·2462 118·40 105·44	..	..	$Pb^{+2}+2(BrO_3)^{-1}$ 152·92 (S) 141·08 (A)
$Pb(IO_3)_2$ .. Pb found =37·22% Pb theory =37·15%	236	0·2356 .. 131·20	..	..	$Pb^{+2}+2(IO_3)^{-1}$ 173·66 (S) 161·74 (A)
$Pb_3(PO_4)_2$ ..	340	0·2239 .. 181·70	..	208·8(4) 184·7(1)	$3Pb^{+}+2(PO_4)^{-3}$ 259·12 (S) 242·78 (A)

TABLE I (*b*)

Lead Salts of Inorganic Acids

Compounds	N	Authors' values	χ_{ma} Computed experimentally	χ_{ma} Computed theoretically
PbC_2O_4 ..	126	0·2416	73·94(4)	$Pb^{+2}+(C_2O_4)^{-2}$
Pb found =70·18% ..		..		77·90 (S)
Pb theory =70·20% ..		71·32		77·60 (A)
$Pb(HCOO)_2$ ..	128	0·2439	79·8 (4)	$2Pb^{+2}+(HCOO)^{-1}$
Pb found =69·1 % ..		..	70·5 (1)	83·70 (S)
Pb theory =69·7 % ..		72·49		83·40 (A)
$Pb(CH_2COO)_2$ ..	142	0·2839	97·66(4)	$Pb^{+2}+(CH_2COO)_2^{-2}$
Pb found =63·74% ..		..		101·40 (S)
Pb theory =64·10% ..		91·77		101·10 (A)
$Pb(CH_3COO)_2\cdot 3H_2O$ ..	144	0·3573	103·8 (4)	$Pb^{+2}+2(CH_3COO)^{-1}$
		135·50	94·1 (1)	107·20 (S)
		96·62		106·90 (A)
		93·82(1)		
$Pb(CHOHCOO)_2$ ..	158	0·3102	109·8 (4)	$Pb^{+2}+(CHOHCOO)_2^{-2}$
Pb found =58·3 % ..		..		110·6 (S)
Pb theory =58·34% ..		110·30		110·3 (A)
$PbC_6H_4(COO)_2$ ..	166	0·3336	127·14(4)	$Pb^{+2}+C_6H_4(COO)_2^{-2}$
Pb found =55·70% ..		..		126·70 (S)
Pb theory =55·82% ..		123·90		126·40 (A)
$Pb(C_6H_5COO)_2\cdot H_2O$ ..	208	0·4250	181·20(4)	$2Pb^{+2}+(C_6H_5COO)^{-1}$
Pb found =44·1 % ..		198·60		181·30 (S)
Pb theory =44·4 % ..		185·64		181·00 (A)
$Pb(C_6H_4OHCOO)_2\cdot H_2O$	224	0·0485	191·38(4)	$2Pb^{+2}+(C_6H_4OHCOO)^{-1}$
Pb found =40·9 % ..		208·90		190·5 (S)
Pb theory =41·5 % ..		195·94		190·2 (A)
$Pb_3[CH_2COO\cdot C(OH)COO$ $CH_2COO]_2 3H_2O$	440	0·3437	296·34(4)	$3Pb^{+2}+2(CH_2COOCOH\,COO$ $CH_2COO)^{-3}$
Pb found =58·80% ..		330·80		307·60 (S)
Pb theory =58·98% ..		291·92		306·70 (A)

studied by Kido and its value has been entered in column 3 along with the authors' values. The specific and the molecular susceptibilities of the hydrated and the anhydrous salts are given one below the other in column 3 of Table I. The molar susceptibilities of salts were also obtained by adding up the susceptibility values of the cations and the anions according to the method followed by Angus and Farquharson.[3] They are given in column 6 of Table I, and are marked as (S) and (A) according as Slater's and Angus' values are used. All the susceptibility values are expressed in -1×10^{-6} c.g.s. units.

Discussion of Results

It will be seen that in many cases values calculated according to Angus and Farquharson's[3] method do not agree with the experimental values. The observed differences are probably due to bond effects which have not been taken into consideration while calculating the susceptibility values of ions. This is borne out by the fact that there is definitely a better agreement in the case of organic compounds where the anion values have been computed by using Pascal's corrective constants than in the case of inorganic ones where purely theoretical values are used. There is a very good agreement between the experimental values of the authors and those calculated by using the values for the anions and the cations obtained by the same investigator (column 5).

(*a*) *Comparison of lead salts with those of barium and thallium*

Lead ordinarily behaves as a bivalent element giving salts isomorphous with those of bivalent alkaline earth metals, particularly those of barium. There is a marked resemblance in the physical properties such as crystalline form and stability of salts like chromates, oxalates, sulphates and phosphates of the two elements. Prasad, Dharmatti and Gokhale[4] have shown that on plotting the values of χ_{ma} against ΣZ for salts of calcium a pattern is obtained which is repeated in the case of the same salts of strontium and barium which are chemically similar. Hence values of χ_{ma} were plotted against ΣZ for the same salts of bivalent lead and barium. These curves are shown in Fig. 1.

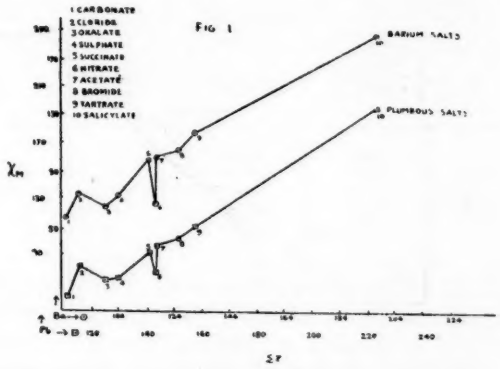
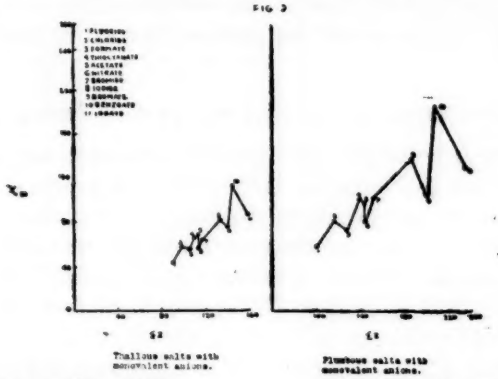


FIG. 1

The striking similarity between the two curves indicates the analogy between the two elements as suggested by the properties mentioned above.

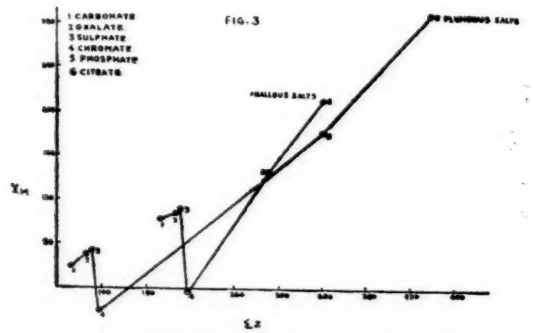
Mellor[27] has pointed out similarity in physical properties of thallous and plumbous salts, such as appearance, specific gravity, hardness, melting point and electrical conductivity, and in their chemical behaviour, such as sparingly low solubility, the colour of the halides and chromates and the behaviour of aqueous solutions towards zinc. Electronically, the thallous and the plumbous ions possess identical electronic shells but differ only in atomic numbers. This analogy between the two elements has been further brought out by the identical patterns of the graphs between χ_{ma} and ΣZ shown in Figs. 2 and 3. In drawing these graphs a distinction has been made



Thallous salts with monovalent anions

Plumbous salts with monovalent anions

FIG. 2



Thallous and plumbous salts with Di- and trivalent anions

FIG. 3

between the salts of monovalent anions and those of divalent anions since the valencies of the plumbous and thallous ions are two and one respectively.

(*b*) *Ikenmeyer's relation*[6]

It will be seen from Fig. 1 that the plot of χ_{ma} against ΣZ is not a straight line and hence the Ikenmeyer's relation ($-\chi_M = C_1N + C_2$) does not hold in the case of plumbous salts. Same general conclusion has been drawn from the study of the several salts of some cations from this laboratory. However it was observed in the case of plumbous salts that if the values of χ_{ma} for (i) organic salts, (ii) $PbCl_2$, $PbBr_2$, PbI_2 and $Pb(CNS)_2$ and (iii) $PbSO_4$, $PbCO_3$, $Pb(NO_3)_2$, $Pb(IO_3)_2$ and $Pb(BrO_3)_2$ are separately plotted against ΣZ the curves obtained are straight lines. The inclinations (C_1) and the intercepts (C_2) of these straight lines on χ_{ma} axis are given below:

	C_1	C_2
(i)	$1{\cdot}32 \times 10^{-6}$	$-95{\cdot}37$
(ii)	$0{\cdot}75 \times 10^{-6}$	$-6{\cdot}00$
(iii)	$0{\cdot}57 \times 10^{-6}$	$-3{\cdot}54$

It may therefore appear that Ikenmeyer's relation holds for definite groups of anions. Further work concerning the elucidation of this viewpoint and assigning meanings to the values of C_1 and C_2 is in progress in this laboratory.

(*c*) *Electronic Isomers*

Values of the molecular susceptibilities of some of the lead salts were calculated, wherever possible, according to Bhatnagar and Mathur's[7] equation for electronic isomers, and are given in the following table.

TABLE II

No. of atoms	Total electrons	Electronic isomers	χ_{ma}(obs.)	Radius in Å. U.	K	χ_{ma}(cal.)
5	112	$TlNO_3$ $PbCO_3$	56·50 60·36	2·63 2·45	2·87	49·1
6	130	$TlClO_3$ $PbSO_4$	72·50 73·36	3·08 2·94	2·68	.. 66·0

It will be seen from the Table that the calculated and the observed values differ from each other by amounts larger than the experimental error and hence lend support to similar conclusions arrived at by Prasad and co-workers.

(*d*) *Ionic susceptibility of plumbous ion*

The ionic susceptibility of the plumbous ion was determined by the same method as followed by Prasad and co-workers.[2] Various values of

TABLE III (*a*)

$\chi_{Pb^{++}}$ from Salts of Inorganic Acids

Compounds	χ_{ma}	χ_{anion}	$\chi_{Pb^{++}}$
$Pb(BrO_3)_2 \cdot H_2O$ ..	105·44	39·6 (1)	26·24
		35·6 (8)	34·24
$PbBr_2$ ..	101·90	34·7 (9)	32·50
		33·9 (10)	34·10
		34·8 (6)	32·30
		30·5 (4)	40·90
		32·5 (11)	36·90
		31·0 (12)	39·90
		33·9 (13)	34·10
		37·1 (1)	27·70
		31·4 (14)	39·10
$PbCO_3$ ..	60·36	22·20(4)	38·16
		28·10(1)	32·26
		24·59(5)	35·77
		29·50(8)	30·86
$PbCl_2$ ..	81·30	23·10(10)	35·10
		22·10(1)	37·10
		20·40(6)	40·50
		20·10(4)	41·10
		20·00(12)	41·30
		23·10(13)	35·10
		23·10(15)	35·10
		22·20(16)	36·90
		21·90(11)	38·50
		25·30(17)	30·70
		24·00(17)	33·30
		24·20(18)	32·90
		19·50(19)	42·30
$PbCrO_4$ ..	18·18	+21·86(20)	40·04
		+33·00(8)	51·18
$Pb(IO_3)_2$ ..	131·20	45·00(21)	41·20
		47·40(8)	36·40
		47·30(22)	36·60
		46·75(5)	37·70
		52·20(1)	26·80
PbI_2 ..	139·20	49·5 (10)	40·20
		53·20(1)	32·80
		44·60(4)	50·00
		49·25(6)	40·70
		50·20(11)	38·80
$Pb(NO_3)_2$ ..	76·85	20·10(1)	36·65
		18·00(12)	40·85
		18·40(23)	40·05
		18·10(22)	40·65
		19·50(22)	37·85
		17·79(5)	41·27
		14·20(4)	48·45
		18·90(8)	39·05

TABLE III (*a*)—(*Contd.*)

Compounds	χ_{ma}	χ_{anion}	$\chi_{Pb^{++}}$
$Pb_3(PO_4)_2$ ..	181·70	35·40(4) 40·43(5) 47·20(1) 43·49(4)	36·97 33·61 29·10 31·57
$PbSO_4$ ..	73·36	33·60(4) 39·00(1) 39·00(8) 37·50(5) 40·10(8) 37·00(8)	39·76 34·36 34·36 35·86 33·26 36·36
$Pb(CNS)_2$ ..	100·60	30·00(8) 38·00(1)	40·60 24·60
$PbBi_2O_3$ ..	83·60	43·00(1) 43·40(4)	40·60 40·20

TABLE III (*b*)

$\chi_{Pb^{++}}$ from Salts of Organic Acids

Compounds	χ_{ma}	χ_{anions}	$\chi_{Pb^{++}}$	Mean $\chi_{Pb^{++}}$
$Pb(CH_3COO)_2 \cdot 3H_2O$ ..	96·62	28·90(4) 32·00(1) 30·00(8) 30·00(21) 29·80(22) 28·76(4) 31·40(1) 30·20(22)	38·82 32·62 36·62 36·62 37·02 39·10 33·82 36·22	36·36
$Pb(C_6H_5COO)_2 \cdot H_2O$ ..	185·64	67·60(4) 66·10(8)	50·44 53·44	51·94
$Pb_3\left(\begin{matrix}CH_2-COO\\ \vert\\ COH-COO\\ \vert\\ CH_2-COO\end{matrix}\right)_2 \cdot 3H_2O$ ..	291·92	79·17(4)	44·53	44·53
$Pb(HCOO)_2$ ..	72·49	16·90(4) 20·20(1) 17·30(22) 17·60(22)	38·69 32·09 37·89 37·29	36·49
PbC_2O_4 ..	71·32	27·94(4) 28·50(21)	43·38 42·82	43·10
$PbC_6H_4(COO)_2$ ..	123·90	81·14(4)	42·76	42·76
$Pb(C_6H_4[OH]COO)_2 \cdot H_2O$ ..	195·94	72·69(4)	50·56	50·56
$Pb(CH_2COO)_2$ ..	91·77	51·66(4)	40·11	40·11
$Pb(CHOHCOO)_2$ ..	110·30	63·80(8) 60·88(4)	46·50 49·42	47·96

anions used are taken from literature and are given in column 3 of the Tables III (*a*) and III (*b*). Values of $\chi_{Pb^{++}}$ thus obtained are given in the last column of these tables.

Two separate mean values of $\chi_{Pb^{++}}$ were taken, one for the values deduced from plumbous salts of inorganic acids and the other for those deduced from salts of organic acids. These mean values are 36·83 and 40·94 respectively. It will be seen from these values that the value deduced from plumbous salts of organic acids is significantly higher than the one obtained from salts of inorganic acids. This difference was statistically established by the standard method. These results are in agreement with those obtained by Prasad, Dharmatti and co-workers, in the case of Ca, Sr and Ba. If, however, the mean values of $\chi_{Pb^{++}}$ deduced from individual organic salts are examined, it will be observed that the values found from formate and acetate agree fairly well with the mean value deduced from inorganic salts. In other cases the values of $\chi_{Pb^{++}}$ obtained are fairly high.

It can be seen from Table III (*b*) that the value of $\chi_{Pb^{++}}$ roughly increases with the number of carbon atoms in the anion. Trew,[8] who also observed such an increase, attributes it to the increase in the effective ionic radius of the cation which results from an increase in the size of the anions. These observations can also be explained on the basis of equilibrium inter ionic distances in a compound which again depend on (i) co-ordination number, (ii) radius ratio, (iii) amount of covalent bond character and (iv) crystal structure.

(*e*) *Susceptibility and Co-ordination[24] Number*

Trew[8] has argued that according to Goldschmidt's theory regarding the influence of the co-ordination number on the interatomic distances and hence on the diamagnetic susceptibility, the diamagnetic susceptibility of a cation in combination with a univalent anion should be greater than that deduced from salts of anions of higher valencies. She found that the mean diamagnetic susceptibility of thallous ion deduced from salts containing univalent anion is $-38{\cdot}4 \times 10^{-6}$ while that deduced from salts containing divalent and trivalent anions is $-37{\cdot}4 \times 10^{-6}$. According to her these results support Goldschmidt's theory. Similar data were collected by the authors in the case of plumbous salts containing (*a*) univalent and (*b*) di- and trivalent anions, and are presented in Table IV.

It will be seen that the mean values of $\chi_{Pb^{++}}$ in the two cases are slightly different but the difference is not statistically significant. Hence it cannot be said with any definiteness that the results given in this paper for plumbous salts support Goldschmidt's hypothesis.

TABLE IV

(*a*) *Salts with Univalent Anions*

Compounds	$\chi_{Pb^{++}}$	Mean $\chi_{Pb^{++}}$
$Pb(NO_3)_2$ ..	40·60	
$PbCl_2$ ..	36·91	
$PbBr_2$ ..	35·28	
PbI_2 ..	40·50	37·12
$Pb(IO_3)_2$ ..	35·74	
$Pb(BrO_3)_2$ ..	30·24	
$Pb(CNS)_2$ ..	40·60	

(*b*) *Salts with di- and trivalent anions*

$PbSO_4$ ..	35·66	
$PbCO_3$ ..	34·26	
$PbCrO_4$ ..	45·61	37·75
PbS_2O_3 ..	40·40	
$Pb_3(PO_4)_2$ ..	32·81	

(*f*) *Theoretical and Experimental Ionic Susceptibilities*

The susceptibility values of Pb^{++} according to Slater's and Angus' methods are 50·2 and 49·9, respectively. Employing the mass susceptibility data for plumbous compounds quoted in the I.C.T. (Vol. VI, page 357), Trew finds the susceptibility for the plumbous ion to be 44·3. She considers that this value is probably high "due to the tendency to convalency" in plumbous compounds. According to her, the value of the plumbous ion deduced from strictly polar compounds should be 38·0. This value agrees fairly well with the experimental value, 36·83, deduced from inorganic salts which is slightly less than 4/5 of the theoretical value. In the case of the thallous ion, which is an electronic isomer of Pb ion, Trew[8] observes that the experimental value was less than $\frac{2}{3}$ of the theoretical value. However, Prasad, Dharmatti and co-workers[2] have found that in the case of calcium, strontium and barium ions, the ionic susceptibilities deduced from the inorganic salts are in fair agreement with the theoretical ones determined by the methods of Slater and Angus. Brindley[25] has observed that there is an increasing divergence between the theoretical and experimental susceptibilities with the increasing atomic weight of the element concerned. This is, however, not borne out from the results obtained in the case of barium. The discrepancies noticed in the case of plumbous and thallous ions and those observed by Brindley suggest that some modification in Slater's method of calculation, probably in the evaluation of the screening constants, is necessary.

(g) *Ionic Radius*

The ionic radius of Pb^{++} has been calculated from the mean ionic susceptibilities, from inorganic as well as organic salts. The results are given below:

TABLE V

Radius of Pb^{++} ion

From χPb^{++} deduced from Inorganic Salts	From χPb^{++} deduced from Organic Salts	From X-ray data (Goldschmidt's value)
1·260 Å.U.	1·328 Å.U.	1·320 Å.U.

It will be seen that the experimental values agree very well with Goldschmidt's[24] value of Pb^{++} from X-ray data.

REFERENCES

1. Kido .. *Sci. Rep. Toh. Imp. University*, Series I, 1932, **21**, 149, 869; 1933, **22**, 835.
2. Prasad and co-workers .. *Proc. Ind. Acad. Sci.*, 1942, **15**, 307; 1944, **20**, 224.
3. Angus and Farquharson .. *Proc. Roy. Soc.*, 1932, **136 A**, 569, 578.
4. .. *I. C. T.*, Vol. VI.
5. Prasad and Desai .. Private communication.
6. Ikenmeyer .. *Ann. der Phys.*, 1929, **1**, 5, 190.
7. Bhatnagar and Mathur .. *Phil. Mag.*, 1928, **6**, 217.
8. Trew .. *Trans. Farad. Soc.*, 1936, **32**, 1658; 1941, **37**, 476.
9. Kido .. *Chemical Soc., Annu. Rep.*, 1941, **38**, 36.
10. Hocart .. *Physical Principles and Applications of Magneto-Chemistry*, by Bhatnagar and Mathur, p. 142.
11. Reicheneder .. *Ann. der Phys.*, 1929, **3**, 60.
12. Sugden .. *J. C. S.*, 1932, 164.
13. Weiss .. *Compt. Rend.*, 1930, **190**, 95.
14. Farquharson .. *Trans. Farad. Soc.*, 1941, **37**, 476.
15. Abbonnene .. *Compt. Rend.*, 1934, **198**, 2237.
16. Leiterer .. *Zeits. Phys. Chemie*, 1937, **36**, 332.
17. Brindley .. *Magnetism and Matter*, by Stoner, p. 271.
18. Hoare and Brindley .. *Trans. Farad. Soc.*, 1941, **37**, 476.
19. Joos .. *Magnetism and Matter*, by Stoner, p. 269.
20. Bhatnagar, Prakash and Hamid *J. C. S.*, 1938, 1428.
21. Hollens and Spencer .. *Ibid.*, 1935, 495.
22. Rao and Shreeraman .. *Phil. Mag.*, 1937, **24**, 1034.
23. Raichaudhari and Sengupta .. *Ind. Jour. Phys.*, 1936, **10**, 2537.
24. Goldschmidt .. *Trans. Farad. Soc.*, 1929, **25**, 253.
25. Brindley .. *Phil. Mag.*, 1931, **11**, 786.
26. Mellor, A. .. *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vols. V and VII.

991-47. Printed at The Bangalore Press, Bangalore City, by G. Srinivasa Rao, Superintendent and Published by The Indian Academy of Sciences, Bangalore